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EDIBLE OILS AND FATS

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Cacao Pods

Frontispiece

THE CHEMISTRY AND EXAMINATION OF

EDIBLE OILS AND FATS

THEIR SUBSTITUTES AND ADULTERANTS

by

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PREFACE

It would be difficult at this time, even if it were advisable, to write a book on the chemistry and examination of oils which is entirely different from its predecessors. It is hoped, however, that the following pages contain sufficient that is new both in material and method of treatment to justify their publication.

An attempt has been made to keep all that is best in method both old and new, and whilst due weight has been given to older work, which the test of experience has shown to be of value, special attention has been given to all the latest methods which hold out promise of usefulness.

The examination of oils has for long suffered from the disadvantage that its methods have been, to a large extent, empirical, but there are welcome signs that such a statement will soon cease to describe truthfully the position. Already many valuable investigations of fundamental importance have been concluded, whilst others are still under consideration. It is considered that the importance of these, merits their treatment in full.

Some methods have been mentioned that up to now have not yielded very useful results. They have been included because they contain, in many instances, some ideas which may be found to be of value in other directions. Many suggestions are also given of subjects for investigation which are likely to yield interesting and valuable results.

It is hoped that the unusually large number of references will be found to be of value. In nearly every case they have been checked from the proofs with their respective Journals. References to abstracts in the *Analyst* and in the *Journal of the Society of Chemical Industry* have been given preference wherever these are available, as these Journals are found in nearly every laboratory, whilst those readers desiring further information will readily find the original sources from these abstracts.

It is with great pleasure that the Author acknowledges the assistance that he has received from many sources. He is indebted to firms and individuals for the loan of blocks, due acknowledgment of which is given in the text. He is greatly indebted to Mr E. R. Bolton and to Mr C. A. Mitchell; to Mr A. W. Knapp for reading the MS. of the chapter on Cacao Butter and for many valuable suggestions, and to Mr J. A. L.

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The preparation of the typescript for the printer was undertaken by Mr H. Holden with energy, ability and painstaking care.

G. D. E.

LIVERPOOL, *July*, 1926.

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EDIBLE OILS AND FATS

EDIBLE OILS AND FATS

CHAPTER I

INTRODUCTION

Oils and fats have been recognised as a class from the very earliest times although they were mostly so described from their physical appearance rather than from any knowledge of their constitution. It would seem probable that the animal fats would be the first to be recognised on account of their ease of preparation and their existence as by-products in prehistoric cookery, whilst in the very earliest records of European civilisation the olive, from which olive oil was separated, at first by hand pressure and later by crude wooden presses, has been regarded as symbolic of peace and plenty.

All down the ages they have been recognised as of great importance as an article of diet and have been an important article of commerce since the appearance of the first traders. As the centuries have passed they have become of increasing importance until at the present moment the industry is world wide, requiring for its transactions vast capital and expenditure, and millions of workers. Large tracts of tropical and sub-tropical countries are given over to the cultivation of oil seeds from which oils are extracted, whilst, particularly in America, millions of animals are slaughtered annually to provide—with other products—lard and tallow.

The distinction between oils and fats is merely a physical one, oils being those oleaginous substances which are fluid at the mean annual temperature, whilst those solid at this temperature are called fats. It thus follows that what may be an oil in one country may be a fat in another. Thus palm oil or coconut oil have the consistency of fats in temperate climates, whilst most oils become more or less crystalline before the freezing-point of water is reached.

The true oils and fats form one large family, all the members of which have an analogous composition, which differs sharply from other substances of somewhat similar physical appearance. It has sometimes happened that these deceptive physical properties have led to the giving of erroneous commercial names to such substances, for instance, sperm oil has not the chemical composition of an oil, but is one of the family of waxes, whilst japan-wax is a true fat having a similar composition to lard or tallow.

The Classification of Oils and Fats.—Various methods of classification have been suggested, based upon one or another of their chemical or physical properties. The ideal method of classification has yet to be suggested, but, in our present uncertain state of knowledge concerning their chemical composition and constitution, that due to Lewkowitsch is probably as satisfactory as any that can be devised.

I. VEGETABLE OILS AND FATS

A. Vegetable Oils

1. Drying oils.
2. Semi-drying oils—
   (*a*) Cotton-seed oil group.
   (*b*) Rape-oil group.
3. Non-drying oils—
   (*a*) Almond-oil group.
   (*b*) Olive-oil group.
   (*c*) Castor-oil group.

B. Vegetable Fats

1. Chaulmoogra-oil group.
2. Laurel-oil group.
3. Palm-oil group.
4. Myristica group.
5. Cacao butter group.
6. Coconut-fat group.
7. Dika-fat group.

II. ANIMAL OILS AND FATS

A. Animal Oils

1. Marine animal oils—
   (*a*) Fish oils.
   (*b*) Liver oils.
   (*c*) Blubber oils.
2. Terrestrial animal oils—
   (*a*) Semi-drying oils.
   (*b*) Non-drying oils.

B. Animal Fats

1. Drying fats.
2. Semi-drying fats.
3. Non-drying fats—
   (*a*) Body fats.
   (*b*) Milk fats.

The Occurrence and Preparation of Oils and Fats.—In nature oils and fats occur widely distributed in enormous quantities, whilst the amount under cultivation is increased year by year. The vegetable fats occur, as a rule, in the fruits of plants—sometimes in the seeds as in palm-kernel oil, at other times in the fleshy pericarp as palm oil. Large tracts of country are under cultivation in various parts of the world for the production of the fruits from which the oils are produced—linseed, flax, cotton-seed and palm are notable examples of these—and each year brings the discovery of new products which may eventually take an important part in the industry. Animal oils and fats, which term, in its widest sense, includes the liver and body oils of fish, are obtained in enormous quantities from hogs, sheep and oxen, whilst the fish-oil industry produces vast amounts of cod-liver and other liver oils and thousands of tons of the oil from seals, whales and other sea animals.

Preparation of Vegetable Oils.—Vegetable oils nearly always occur embedded in cells in the plant tissue, and some process is, therefore, necessary to remove the oil from the plant in order to prepare it for use. In the earliest times the few recognised vegetable oils were prepared by hand pressure, and later, by crude wooden presses, but at the present time oils may be extracted by hydraulic pressure, by heat, by grinding, or by the use of volatile solvents. The oils used for technical purposes do not require particular care in their preparation, but where, as in edible oils, good colour and flavour are essential, the greatest care has to be taken from the very gathering of the seeds.

In some cases, and the amount of oil so produced will doubtless increase year by year, the oil is expressed from the seeds immediately these are gathered, but where this is not the case great care must be taken in the transportation and storage of the seeds so that they are kept free from moisture and also from light. The seeds should also be loosely packed, so that no heating action takes place. The flavour of the oil may be seriously impaired by fermentation or other changes occurring in the seed during storage. This question of storage is receiving now much greater attention

than it did in previous years. Several important investigations have been instituted by the Food Investigation Committee concerning the storage of fish and fruit—it would undoubtedly be an advantage for similar investigations to be carried out in regard to oil seeds.

Before the actual business of extracting the oil is commenced, the seed is cleaned by the use of screens, a screen of fine mesh being used to remove particles smaller than the seeds, and one having a mesh slightly larger than the seeds which will allow them to pass through, whilst retaining larger impurities. It is also very usual to pass the seeds over magnets which remove any particles of iron which would be deleterious to the machines subsequently used. In some cases the outer coating of the seed is removed before the oil is extracted; this process is known as decortication. The shells are removed by means of revolving knives, which are so adjusted that they cut the shell without injuring the kernels. The shells may then be removed by a strong air current.

Oils of the finest flavour are produced by crushing the cleansed seed and subjecting it to hydraulic pressures in the cold, but for inferior and non-edible oils a much larger yield is obtained by heating the crushed seed in a steam-jacketed pan to about 160°–180° and blowing in steam. The seed so treated is then moulded into cakes of suitable size and submitted to enormous pressures in hydraulic presses. In some cases seeds rich in oil are pressed first in the cold (" cold-drawn " oils) and the residue afterwards heated and re-pressed. The expressed oils are clarified from turbidity due to the presence of mucilage and albuminous matters by allowing them to settle in tanks or by filtering through filter-presses; fuller's earth being frequently used in the last operation. In many cases the oils are further treated (" Refinement ") with special reagents or in a special manner to improve their appearance; heating, freezing, oxidation, reduction and other processes all having their application (cf. B. Hassel, *J.S.C.I.*, 1925, 44, B640).

In many cases the residue from the presses, " oil-cake," is a valuable cattle food, and in such cases the greatest pressures are not used so that a reasonable percentage of oil may be left in the " cakes." Such cakes are sold on the basis of the amount of oil and albuminoids which they contain. The following, among others, are well-known commercial articles: cotton-seed cake (decorticated and undecorticated), linseed cake, coconut cake.

Extraction by solvent gives the largest yield of oil but has some disadvantages owing to the fact that in the past the cakes so produced were practically useless as feeding-stuffs. This method is chiefly used, therefore, in those cases where the pressed cake is not suitable for use as a feeding-stuff, or where, on account of the poor quality of the seed, the production of an oil of good flavour is impossible in any case. It is more than likely, however, that the extraction method will find increasing use, especially as it is not difficult to adjust the extraction in such a way that enough oil is left in the cake for feeding-stuff purposes. The solvents in general use are carbon bisulphide and petroleum ether, whilst carbon tetrachloride and the chlor-ethanes and chlor-ethylenes (Westrosol, etc.), have been proposed more recently, although their comparatively high cost militates against their general use, in spite of their obvious advantages. The extraction is carried out by a process of percolation, the oily solution being evaporated, the oil recovered, and the solvent being used for further extraction. The cake can readily be completely freed from solvent, and is quite as good, apart from the fat question, as expressed cake.

Preparation of Animal Oils and Fats.—The body fats of animals may be

divided into two main divisions, the internal fat and the superficial fat; the intramuscular fat has often different properties from either. These two main divisions are kept separate, as the internal fat is usually considered to be the more valuable, lard, for instance, being probably in the first place the kidney (or leaf) fat of the hog, although the term now has a much wider interpretation. The fat is " rendered " in " digesters," large metal boilers, by means of steam, edible fats usually being treated at moderately low temperatures, but fats intended for commercial purposes are treated with superheated steam at high pressures, whereby the yield is considerably increased. By such treatment the oil is freed from the tissues, floats on the surface of the condensed water and may be recovered. Various oils are treated in more or less special ways—where such are of interest they will be dealt with under the individual substances.

CHAPTER II

PROPERTIES OF OILS AND FATS

Oils and fats vary in physical appearance from a white, wax-like solid to a deep yellow, or even red, somewhat viscous liquid, all of which impart a fixed transparent stain to paper. When in the pure condition, freed from concomitant impurities, they have practically no odour and little taste. The characteristic odours and flavours by which many of the oils and fats are known are really produced by substances occurring with the oils, but of non-fatty chemical constitution.

Melting-point.—This is one of the most difficult determinations to carry out in the examination of oils and fats. The practical details are discussed in Chapter VIII under the general methods of examination. The reasons for the difficulties there referred to are that oils not being definite chemical substances do not melt sharply at some definite temperature, whilst the actual crystalline condition of the substance, on which, of course, will depend its observed melting-point, will depend upon the manner in which it has been stored and the time that has elapsed since it was last in the liquid condition (cf. the two conditions). The melting-points usually given in the literature are open to more or less serious objection, as they are obtained by varying methods; strictly speaking they are of comparative value only and should only be interpreted in terms of other values obtained by the same method. It is highly important that a standard method should be universally adopted by which all such determinations could be made. Typical values for melting-points are given under the individual fats; they may vary between -30° and $+50^\circ$. The melting-point of margarine fat is an important factor.

Boiling-point.—Under normal pressures, oils and fats do not boil without decomposition—neither are they, when freshly prepared, appreciably volatile in steam. Caldwell and Hurtley, however, by using the vacuum of the cathode light (*Proc. Chem. Soc.*, 1909, 25, 73) have been able to subject various oils to fractional distillation without decomposition, and have obtained some interesting results. These results, together with those of other workers, will be discussed later under the general composition of oils and also under the oils in question.

Solubility.—Oils and fats are insoluble in water, and only slightly soluble in cold alcohol. Castor oil is an exception to the latter, this property being made use of as a test for the oil (cf. page 456). They are soluble to varying extents in hot alcohol and hot glacial acetic acid, tests for oils based upon these two properties having been devised by Crismer, Valenta and others. These tests are described under general methods of examination, page 89. They are readily soluble in petroleum ether, ether, chloroform, carbon bisulphide, carbon tetrachloride, benzene, the chloro-ethanes and the chloro-ethylenes, the solubility of these latter compounds having been investigated by Gowing-Scopes (*Analyst*, 1910, 35, 238; 1914, 39, 4 and 385).

Specific Gravity.—All oils and fats are less dense than water, their specific gravity at $15{\cdot}5^\circ$ varying between 0·910 and 0·970; the various methods available for this determination are described in the later sections. The

temperature for oils is usually 15·5° compared with water at the same temperature, but varying temperatures are used for fats. These are mentioned in the appropriate tables.

Refractive Index.—The refractive index of oils and fats is better taken at 40°, as practically all of them are liquid at that temperature. A temperature of 25° has been recommended by the International Conference on Food Analysis for oils, with a temperature of 40° for all fats not liquid at 25°. There seems to be no object in having this dual temperature, as a temperature of 40° is equally convenient for both, whilst the use of one temperature makes it possible to compare the figures for various different substances, at the same time making necessary only one setting of the temperature of the refractometer. At 40° the refractive index of edible oils and fats varies between 1·448 and 1·474. Where figures in the literature are not given at this temperature a correction must be applied to bring the figures to this temperature. This has been variously given by different observers. Richmond (*Analyst*, 1907, 32, 44), examining the results of Tolman and Munson, Delaine and Leach, gives the most probable value as 0·00038 for each degree, the index of refraction rising as the temperature falls. Wright (*J.S.C.I.*, 1919, 38, 392T) gives the correction in terms of a factor. He states that the refractive index at 40° can be calculated from that at any other temperature by subtracting one from the refractive index and multiplying the difference by the factor in the following table opposite the temperature at which the determination was made, and then adding one to the product so obtained.

TABLE I.—CHANGE IN REFRACTIVE INDEX WITH TEMPERATURE

TEMP. °C.	FACTOR	TEMP. °C.	FACTOR
15	0·98078	40	1·00000
15·5	0·98116	41	1·00078
20	0·98457	42	1·00157
25	0·98838	43	1·00236
26	0·98914	44	1·00314
27	0·98991	45	1·00393
28	0·99068	46	1·00472
29	0·99145	47	1·00552
30	0·99222	48	1·00631
31	0·99299	49	1·00710
32	0·99377	50	1·00790
33	0·99454	51	1·00870
34	0·99532	52	1·00950
35	0·99610	53	1·01030
36	0·99687	54	1·01110
37	0·99765	55	1·01190
38	0·99843	60	1·01593
39	0·99922	65	1·02000
40	1·00000	70	1·02408

These factors are criticised by Joseph (*J.S.C.I.*, 1920, 39, 66T) as being unnecessarily complicated ; he advises the factor 0·00036 for each degree, which does not compare too favourably with the 0·00038 given by Richmond. The factor is not, of course, quite the same for all oils, but a mean figure

may be taken as 0·00037 where the correction to be applied is only small. Cf. Roberts, *Analyst*, 1916, 41, 376; Liverseege, *ibid.*, 1919, 44, 48; Richmond, *ibid.*, 1919, 44, 167; Thompson, *ibid.*, 1922, 47, 469; Harvey, *ibid.*, 1923, 48, 19; Rhodes and Goldsmith, *ibid.*, p. 506.

The refractive index has been suggested coupled with the melting-point as a means of establishing the composition of mixtures of various oils. The figures obtained from an examination of a series of mixtures are given by Trim (*J.S.C.I.*, 1920, 39, 307T). These tables show in full detail how the refractive indices of mixtures vary with the composition.

An interesting account of the relation between the refractive index and the other constants of oils, particularly the iodine value, is given by Pickering and Cowlishaw (*J.S.C.I.*, 1922, 41, 74T). They find that the refractive index may be given by the following equation:

$$n_D = 1{\cdot}4643 - 0{\cdot}000066\ (\text{S.V.}) - 0{\cdot}0096\ (\text{A.V./S.V.}) + 0{\cdot}0001171\ (\text{I.V.})$$

where S.V., A.V., and I.V. are the saponification value, acid value and iodine value respectively. Further work on these lines may yield valuable results (cf. J. Lund, *J.S.C.I.*, 1922, 41, 944A). The chief value, however, to the analyst of the refractive index lies in the ease with which the determination can be carried out and in the small quantity of oil necessary. In the examination of oils and fats the refractive index has definite diagnostic value.

Optical Activity.—The majority of oils and fats show very little optical activity, the chief exceptions being castor and chaulmoogra oil, neither of which, of course, are edible, except the former in the medicinal sense. Lewkowitsch has, however, pointed out that when a new fat appeared on the market under the name of "Morotti Oil," which had been used in the manufacture of margarine and produced toxic effects, the optical rotation of a sample of the margarine at once enabled the cause of the trouble to be traced. He adds that it seems advisable, therefore, not to omit the examination of new oils and fats for optical activity, as it is not unlikely that a larger number of optically active fats may occur in nature than has been observed hitherto.

The optical activity of most of the oils is due to the presence of small quantities of such optically active substances as the sterols, but that of those oils having a high value is due to the presence of optically active glycerides. Full details of all these will be found in the appropriate places.

Microscopic Appearance.—Oils and fats are not generally examined under the microscope, but various special methods of examination for lard, butter, coconut oil, etc., are somewhat valuable and will be found mentioned in their respective places. The methods, however, require very careful technique and the results obtained must be treated with more or less suspicion unless the operator has had very considerable experience.

Viscosity.—The viscosity of an oil is not of any great importance from the point of view of the examination of edible oils, but for those oils likely or destined to be used as lubricants it is of the greatest value. It is not usual in commercial transactions to express the viscosity of oils in absolute units, but to give comparative results which have been obtained by some standard instrument, such as the Redwood Viscosimeter, the use of which is described in Chapter VIII, page 102. Castor oil has a very high viscosity as compared with the other seed oils, all of which give figures of a similar order, though they have considerable variation among themselves.

Rancidity.*—Most oils and fats after they have been kept for some time

* Cf. articles by T. W. Jones (*Chemistry and Industry*, 1924, 43, 1258), and W. C. Powick (*J.O.F.I.*, 1924, 1, 63).

develop an objectionable odour and taste—such oils are said to be rancid. A vast amount of work has been devoted to the elucidation of this change, but even now it cannot be said that the phenomenon is at all thoroughly understood. Lewkowitsch ascribes the primary cause of rancidity, the formation of free fatty acids, to the action of moisture in the presence of soluble ferments, enzymes, which act as catalysts. The presence of free fatty acids, however, does not alone produce rancidity, and there is now no doubt that more fundamental changes take place before the oil becomes definitely rancid. In a recent paper, Bevis (*J.S.C.I.*, 1923, 42, 417T) summed up the present state of our knowledge in the following way: " Most investigators agree that the action of air is essential in promoting the decomposition. Lewkowitsch (*J.S.C.I.*, 1903, 22, 68) defines as rancid those oils and fats the free acids of which have been oxidised by the oxygen of the air in the presence of light. On the other hand, Wagner, Walker and Oestermann (*J.S.C.I.*, 1913, 32, 759) found that fats kept in an atmosphere of nitrogen for two years and exposed to the light, became rancid, and concluded that light is the determining factor in the development of rancidity. D. C. Dyer (*J. Agri. Res.*, 1916, 6, 927) analysed the air contained in butter before and after cold storage and found that the oxygen content decreased and the carbon dioxide content increased, indicating oxidation changes in the fat. The quantity of carbon dioxide found was directly proportional to the amount of non-fatty material present in the butter, and the conclusion was drawn that the unpleasant flavours of rancid butter are produced by the oxidation, not of the fat itself, but of the non-fatty ingredients. W. N. Stokoe (*J.S.C.I.*, 1921, 40, 75T) in work on butter and margarine fats, concluded that rancidity is due to the products of oxidation and hydrolysis, the chief factors being moisture, light and air, assisted by traces of lipolytic enzymes which may be present in the fat. Scala (*Gazz. Chim. Ital*, 1908, 38, 307) isolated the decomposition products of rancid fat, and by oxidation with potassium permanganate was able to obtain acids which were separated by means of their barium salts. These acids were identified as œnanthylic, pelargonic, butyric, caprylic and capric acids, and the conclusion was drawn that rancidity is caused by the presence in the fat of the aldehydes corresponding to these acids. It is on the presence of these oxidisable aldehydes that the (chemical) tests for rancidity depend. Most investigators agree that the decomposition proceeds in two stages, (1) hydrolysis of the glycerides and consequent formation of free fatty acid and glycerol, and (2) oxidation of the acid and glycerol thus formed and interaction of the oxidation products, the resulting compounds being responsible for the unpleasant taste and odour of rancid fat.

The author has shown that, in the case of very old samples of cotton-seed oil and fish oils a quantity of volatile acids was produced, the samples having Reichert values of 4·6–11·1, the value being fairly proportional to the acidity (*Year-Book of Pharmacy*, 1913, 573), but these samples were, unfortunately, not further examined. It is interesting to note that the Polenske value had only increased slightly.

Bevis (*loc. cit.*), as the result of a further investigation on animal fats, reaches the following conclusions: " 1. Light greatly accelerates the decomposition of fat at ordinary temperatures. 2. The presence of free oleic acid increases the rate of formation of the compounds causing the Kreis reaction, whilst free glycerin has practically no effect thereon. 3. Increase in free fatty acidity has no relation to the intensity of the Kreis reaction. 4. The Kreis reaction estimates some compounds which are not determined by the Issoglio oxidation method. 5. The appearance of mould

in a fat is accompanied by a marked increase in free fatty acidity. 6. The colouring matter of fats seems to play some part in their decomposition." In regard to this last statement it may be pointed out that as pure glycerides are colourless, the bleaching action of light upon oils must be due to the effect on the colouring matter present in the oil.

Chemical tests for rancidity are not really necessary, as the taste and smell are quite sufficient, except for purposes of quantitative comparison. The modifications due to Kerr (*J. Ind. & Eng. Chem.*, 1918, 10, 471) of the methods of Kreis and Issoglio are, however, added here for the sake of completeness.

The Kreis test is performed by diluting the oil with non-reacting kerosene and recording the limiting degree of dilution at which the red colouration is still produced when 10 c.c. of the mixture is shaken with 10 c.c. of concentrated hydrochloric acid, and the mixture then shaken with 10 c.c. of a 0·1 per cent. of phloroglucinol in ether.

The Issoglio test as modified by Kerr and by Bevis is carried out by heating 25 grams of the fat with 100 c.c. of distilled water for two hours at 100°, with constant shaking, and then filtering through a wet filter-paper. The filtrate is made to 100 c.c. and 10 c.c. is oxidised by boiling for five minutes with a known volume of N/100 permanganate. The flask is cooled, the same volume of N/100 oxalic acid containing sulphuric acid added and then titrated with N/100 permanganate. The oxidisability value is expressed as the number of milligrams of oxygen required to oxidise the water-soluble material in 100 grams of the fat.

Bevis considers the Kreis test to be more sensitive than the Issoglio test.

From the above description of the present state of our knowledge in regard to the rancidity of oils, it will be seen that the best method of storage is to exclude light, moisture and air as far as possible, and to keep the temperature low. It is also important to start with the material as nearly sterile as possible, and to prevent the entry of all types of micro-organisms. The special case of butter and margarine in which non-fatty substances form an appreciable proportion of the whole, will be dealt with under these headings. Cf. H. E. Fierz-David, *J.S.C.I.*, 1925, 44, B105; T. von Fellenberg, *ibid.*, p. B179; A. Azadian, *ibid.*, p. B679.

Drying—Oxygen Absorption.—In the classification given on page 2, the oils and fats are divided into two main classes, drying and non-drying, with an intermediate class described as semi-drying; the meaning of these terms must now be discussed.

When oils of the class described as drying oils, of which linseed oil is a typical example, are exposed to the air, either in the presence or absence of light, they become thicker, whilst after a time a skin forms on the surface which is more or less elastic; this skin gradually becomes thicker as the exposure is continued. The usual method of showing this property is to spread a thin film on squares of perfectly clean glass, allow the plates to stand on their edge for a short time to drain, and then to leave the films so obtained exposed to the air under standard conditions—say in an incubator at 21°, in which is placed a basin containing water, so that the atmosphere may be saturated with moisture—and observing the appearance from time to time. The films so prepared are (in the case of good drying oils containing no adulterants) more or less elastic and transparent, and not only insoluble in water and alcohol, as the original oils are, but are also only very slightly soluble in ether. This latter property has been made use of by Elsdon and Hawley (*Analyst*, 1913, 38, 3) as a quantitative measure of the drying power, and as a method for detecting adulteration; it is described in a later

section. The non-drying oils under similar conditions remain practically unchanged, whilst the semi-drying oils occupy an intermediate position.

This property is much hastened by the presence of various substances such as litharge, manganese resinate, etc., technically known as "driers," and for this reason they are added to paints, varnishes, boiled oils, etc., to promote the speedy production of a film. This fact is further made use of in some of the quantitative methods for the determination of oxidation which are described later. The chemistry of the drying oils, with particular reference to the constitution of linoxyn, has been considered at length by G. W. Ellis (*J.S.C.I.*, 1925, 44, 401T, 463T, 469T, 486T); cf. also *The Chemistry of Drying Oils*, Morrell & Wood. London: Ernest Benn, Ltd.

This power of drying, or of oxidation, is intimately connected with the power of absorbing iodine which is discussed later; the further elaboration of the causes is discussed in the next paragraph. Cf. "The Autoxidation of Fats, etc.," A. Tschirch, *J.S.C.I.*, 1925, 44, B251, and "The Polymerisation of Fatty Oils," J. Marcusson, *ibid.*, p. B250, and H. Wolff, *ibid.*, p. 290. "The Measurement of the Susceptibility of Fats to Oxidation," Greenbank and Holm, *Analyst*, 1925, 50, 463.

Halogen Absorption.—Some of the radicles of the fatty acids contained in the glycerides of fats are unsaturated—the typical example is oleic acid, which is described on page 32. Under these circumstances it will be naturally assumed that, following the example of the simple unsaturated compounds, these glycerides will be capable of combining with halogens; this has been found to be the case to a greater or less extent. In the case of chlorine and bromine the combination (substitution also takes place) is direct and often violent (cf. bromine thermal value, page 37), in the case of iodine, the direct reaction is nearly always slow and incomplete, but by means of adding mercuric chloride to an alcoholic solution of iodine, quantitative results may be obtained (cf. iodine value, page 137).

Although the reaction may at first sight appear to be a simple one, yet, as a matter of fact, it seems to be most complex. Many workers have put forward theories to account, for example, for the rôle played by the mercuric chloride in the Hubl solution, and for these the reader may be referred to the following papers: Wijs, *J.S.C.I.*, 1898, 17, 698; Ingle, *ibid.*, 1902, 21, 587; 1904, 23, 422; 1908, 27, 314; 1913, 32, 639; 1919, 38, 101T. The subject has recently been taken up again by B. M. Margosches and his collaborators, who have published a series of papers (*ibid.*, 1924, 43, B341, B564, B680, B719, B877) on various aspects of the iodine value; this work is being continued.

Oils as Solvents.—A large number of substances are soluble to a greater or less extent in oils, whilst many organic liquids are miscible therewith in all proportions.

Gases are soluble to some extent. According to the determinations of Vernon (*Proc. Roy. Soc.*, 1907, 78, B366*) 100 c.c. of oils will dissolve 2·3 c.c. of oxygen, 5·2 c.c. of nitrogen or 0·2 c.c. of carbon dioxide. The nature of the oil does not appear to have much effect on the solubility, whilst at the two temperatures used, namely 15° and about 40°, the figures are almost identical.

Camphor is readily soluble in liquid oils, the *Linimentum Camphoræ* of the British Pharmacopœia being a 20 per cent. solution by weight of camphor in olive oil.

* *Analyst*, 1907, **32**, 381.

Phosphorus is also moderately soluble in many of the fixed oils. The *Oleum Phosphoratum* of the British Pharmacopœia contains 1 per cent. by weight of phosphorus dissolved in almond oil and flavoured with 1 per cent. of oil of lemon.

The solubility of iodine in oils is greatly complicated by the combination of the solute with the solvent, a subject which is dealt with under iodine value on page 137. Iodine does dissolve to a certain extent in the oil, but it immediately commences to combine, either by addition or substitution (almost entirely by the former) so that it is impossible to determine the actual solubility. Iodine ointment of the British Pharmacopœia usually contains about 3 per cent. of free iodine and about 1 per cent. of combined iodine, although it is actually prepared by the addition of 4 per cent. of iodine.

General Variation in Properties.—It is possibly quite unnecessary to remind the worker in the field of fats that the properties of one particular member are not the properties of one definite substance, but that they are the mean of the properties of the various glycerides of which they are composed. As, therefore, a fat is not a substance of definite composition it follows (almost logically and certainly practically) that the properties of oils from various similar sources, although very much alike, are not identical, and vary according to differences in the variety of the plant, the climate, the soil and the method of cultivation. That these differences occur is not surprising, rather is it a matter for wonder (and congratulation) that they are not greater, although this general agreement rather accentuates the occasional divergencies. These divergencies, although they undoubtedly do occur, are not very frequent, and for ordinary work must be ignored and average figures assumed and worked to. The industrial chemist is, frequently, in a much better position in this connection than the public analyst, as the former has the privilege of returning a sample as " adulterated or abnormal," whilst for the latter the " abnormal " class is not supposed to exist; the public analyst, therefore, will be wise to report " genuine " until he is morally certain that adulteration has taken place.

CHAPTER III

THE COMPOSITION OF OILS AND FATS

The particular nature of fixed oils and fats was first elucidated by Chevreul, in the second decade of the nineteenth century, who, by a long series of experiments, showed that they were compounds of glycerol with organic acids having for the most part a straight carbon chain. Glycerol is, of course, a trihydric alcohol, so that it is possible for three molecules of the acid (called a fatty acid for obvious reasons) to combine with each molecule of glycerol in the following way, R standing for one radicle of fatty acid.

$$\begin{array}{l} CH_2OR \\ | \\ CH\cdot OR \\ | \\ CH_2OR. \end{array}$$

For many years it was more or less assumed that the three molecules of fatty acid attached to the same glycerol molecule were similar, and that the simple glycerides (as such are called) were merely mixed together in the fats. It is obvious, however, that mixed glycerides may be found, and that the following formations, which may be conveniently described as mixed triglycerides, are possible ;

$$\begin{array}{lccccc} (\alpha) & CH_2\cdot OR_2 & CH_2\cdot OR_1 & CH_2\cdot OR_1 & CH_2\cdot OR_2 & CH_2\cdot OR_1 \\ & | & | & | & | & | \\ (\beta) & CH\cdot OR_1 & CH\cdot OR_2 & CH\cdot OR_2 & CH\cdot OR_1 & CH\cdot OR_3 \\ & | & | & | & | & | \\ (\gamma) & CH_2\cdot OR_2 & CH_2\cdot OR_2 & CH_2\cdot OR_3 & CH_2\cdot OR_3 & CH_2\cdot OR_2. \end{array}$$

The positions of the acid groups are characterised by the use of the letters α, β and γ, as shown in the table.

Although the possibility of mixed glycerides had been discussed previously, the first experimental evidence of their probable existence was obtained in the case of butter fat. Tributyrin is quite readily soluble in alcohol, and yet it is not possible to extract any from butter by treatment with alcohol, pointing to the fact that no tributyrin is present, and, therefore, that the contained butyric acid forms part of a mixed glyceride or glycerides. The evidence for the existence of such glycerides in natural fats has been largely increased of late years, and there seems little doubt now but that mixed glycerides constitute the bulk of the fats, and that simple triglycerides are present in relatively small quantities. A number of such mixed glycerides have been prepared synthetically, but the number isolated from natural sources has rapidly increased, and is shown, for example, in the articles on coconut oil on page 330, palm-kernel oil on page 344, lard on page 360.

When glycerides are treated in a variety of ways they split up into glycerol, and the free fatty acids, or, if alcohols or alkalies are used, the appropriate salts of the acids. This change may be shown by the following equation where R represents a radicle of fatty acid and X a positive monovalent radicle.

$$\begin{array}{lcl} CH_2{-}OR & & CH_2OH \\ | & & | \\ CH_2{-}OR & + 3\,X{-}OH = & CH\,OH \\ | & & | \\ CH_2{-}OR & & CH_2OH \end{array} \quad + \quad 3\,R{-}OX$$

Geitel and Lewkowitsch have deduced some evidence to show that the reaction takes place in stages, and that each glyceride loses one acid radicle before the second and third are touched, but E. F. Armstrong and Allan (*J.S.C.I.*, 1924, 43, 209T), report work by Moore which goes to show that trilaurin, at least, is changed at the same rate as monolaurin, and that the hydrolysis does not take place in stages. This problem can hardly yet be looked upon as being settled ; it is still a matter of considerable controversy and further work is required to settle the matter.

The decomposition as given above can be carried out in a variety of ways and with many reagents, these include steam under pressure, acids and alkalies, and alcohols. Although the action of steam has not received any extended use in practice, the action is considerable with pressures of five atmospheres and over. (Kliment, cf. Lascaray and Bergell, *J.S.C.I.*, 1925, 44, B179, B889.) The action of hydrochloric acid has been studied by Lewkowitsch (*J.S.C.I.*, 1903, 22, 67), but has apparently not been used on the commercial scale. The following table contains some of the results of Lewkowitsch.

TABLE II.—HYDROLYSIS OF OILS AND FATS BY MEANS OF HYDROCHLORIC ACID

Sp. Gr. 1·16 (Lewkowitsch)

100 grms. of Oil or Fat and 100 c.c. of Acid ; fresh acid used after each sample had been taken.

Oil or Fat.	Original acid value.	Acid values after						Acid value of completely hydrolysed Oil or Fat.
		2 hrs.	7 hrs.	12 hrs.	16 hrs.	20 hrs.	24 hrs.	
Cotton-seed.	0·35	18·42	79·6	116·2	144·9	164·8	175·8	202
Whale . .	6·01	26·69	101·3	142·7	162·3	172·0	..	195
Rape . .	2·16	19·66	75·06	107·2	127·3	140·3	151·8	185
Lard . .	1·25	14·51	84·78	139·8	152·1	168·0	177·0	201
Tallow . .	11·15	43·39	112·5	153·2	173·3	183·3	186·8	200
Coco-nut .	18·75	79·73	184·2	221·4	233·4	241·1	250·1	260
Castor . .	1·22	44·4	47·3	51·4	47·9	46·8	41·64	190

Concentrated sulphuric acid at temperatures above the boiling-point of water acts very rapidly as the following results by Lewkowitsch (*Oils, Fats and Waxes*, 5th Edit. Vol. I, page 84) show.

TABLE III.—TALLOW HYDROLYSED WITH 4 PER CENT. OF CONCENTRATED SULPHURIC ACID AT 120° C. (LEWKOWITSCH)

	Product contained free fatty acids per cent.
Sample taken after 1 hour's steaming	42·1
,, ,, ,, 2 ,, ,,	65·1
,, ,, ,, 3 ,, ,,	79·3
,, ,, ,, 4 ,, ,,	83·7
,, ,, ,, 5 ,, ,,	88·6
,, ,, ,, 6 ,, ,,	91·7
,, ,, ,, 7 ,, ,,	91·7
,, ,, ,, 8 ,, ,,	92·3
,, ,, ,, 9 ,, ,,	93·0

The rate of hydrolysis can be further hastened by using the Twitchell reagent (English patent 4741 of 1898) which consists of a sulpho-aromatic compound produced from naphthalene. The author is indebted to Warburton for the following method of preparation of this reagent:

100 parts by weight of oleic acid are placed in a dry vessel with 30 parts of naphthalene, the mixture being warmed until solution takes place.

It is then cooled to about 120° F. by continuous stirring in order to prevent the naphthalene settling out in a solid mass at the bottom. At that temperature the naphthalene will crystallise in very fine needles, but this is of no consequence, as it dissolves readily in the acid if the mass is well stirred.

300 parts by weight of sulphuric acid of 66 Be. containing 99·2 per cent. of H_2SO_4 are then weighed off. This should be checked by analysis, as an acid of the same specific gravity, namely 1·8400, may only contain 95 per cent. H_2SO_4.

The acid is run in at first drop by drop as long as a violent reaction takes place (afterwards it may be run in a little quicker), and the mixture kept constantly agitated.

The temperature should be kept below 120° F., if it is allowed to rise to 130° F. or higher the efficiency of the reagent as a fat splitter is impaired.

When all the acid is run in, the mixture is poured into twice the volume of cold water, well stirred, and allowed to settle out overnight; after standing, the reagent will appear as a thick layer on the top of the water, and the clear aqueous layer may be drawn off. The product is then ready for use. The reagent should not be washed again, as a trace of acid is essential to its rapid action.

The conditions of the reaction are discussed by O. Steiner, *J.S.C.I.*, 1925, 44, B138.

The acids as described above act for the most part merely as catalysts, and it has been discovered that many seeds contain organised catalysts or enzymes which hydrolyse the oils occurring there before they are assimilated by the young plant. It is quite possible to isolate these enzymes (lipase) and bring about the hydrolysis of oils on the commercial scale by means of a white powder which can be kept for a considerable length of time without deterioration. This method has been worked out by several investigators, and reference may be made to the following papers: *J.S.C.I.*, 1904, 23,

327, 942; 1910, 29, 1259; 1912, 31, 884, 1084; 1920, 39, 340A. Sudborough, Watson and Varma (*J.S.C.I.*, 1920, 39, 340A), found that by using four parts of crushed castor-seed, 100 parts of oil to be hydrolysed, and 0·2 part of manganous sulphate, 90 to 95 per cent. of the oil is hydrolised in 48 hours. In order to bring about the rapid action of the enzyme it is desirable that the oils be very thoroughly emulsified. As is the case with other catalytic reactions, the process is reversible. (*J.S.C.I.*, 1911, 30, 433, 633, 1395; 1925, 44, B290.)

The most important method of hydrolysis or saponification is by means of bases—the most common laboratory method is with soda or potash, although on the commercial scale lime is largely used. The reaction proceeds according to the following equation.

$$\begin{array}{lcllcl} CH_2OR & & KOH & CH_2{-}OH & & KOR \\ | & & & | & & \\ CH{\cdot}OR & + & KOH = & CH{-}OH & + & KOR \\ | & & & | & & \\ CH_2OR & & KOH & CH_2{-}OH & & KOR \end{array}$$

The amount of potash absorbed in this reaction is a valuable method used in the analytical examinations of oils, and is fully described on page 116. When alcoholic potash is used in place of aqueous potash the final reaction is the same in those cases where the amount of potash present is greater than that required to combine with the fatty acids, but where only small quantities of potash are present the reaction takes a different course, or rather, stops at an earlier stage, with formation of the esters of the fatty acids according to the following equation, in the case of ethyl alcohol.

$$\begin{array}{lcllll} CH_2{\cdot}OR & & C_2H_5OH & CH_2{\cdot}OH & & R{\cdot}O{\cdot}C_2H_5. \\ | & & & | & & \\ CH{\cdot}OR & + & C_2H_5OH & CH{\cdot}OH & & R{\cdot}O{\cdot}C_2H_5. \\ | & & & | & & \\ CH_2{\cdot}OR & & C_2H_5OH & CH_2OH & & R{\cdot}O{\cdot}C_2H_5. \end{array}$$

In these cases the alkali appears to act as a catalyst, and the same reaction may be brought about by the use of hydrochloric, sulphuric or phenol-sulphonic acids. On these reactions is based the method of alcoholysis first proposed by Haller and described on page 51.

In addition to the glycerides which usually constitute well over 95 per cent. of the oil, various other substances may be present such as lecithin, complex alcohols, etc. Lecithin is a complex compound containing phosphorus, having two fatty acid radicles, and one radicle containing phosphoric acid combined with a molecule of glycerin, and may be looked upon as a triglyceride in which one of the fatty acid radicles has been replaced by a complex organic base containing phosphoric acid. The following formula represents the constitution of one of these bodies of which a number from different sources are known.

$$\begin{array}{l} CH_2{\cdot}COOC_{15}H_{31} \\ | \\ CH{\cdot}COOC_{17}H_{35} \\ | \qquad\qquad OH \\ CH_2{\cdot}O{-}P{=}O \\ \qquad\qquad\quad O{\cdot}CH_2{\cdot}CH_2 \\ \qquad\qquad\qquad\qquad\quad N(CH_3)_3. \\ \qquad\qquad\qquad\qquad HO \end{array}$$

Lecithin is soluble in alcohol and may be recrystallised therefrom at suitable strengths. It is insoluble in acetone and various esters such as ethyl acetate. The amount of lecithin present in a sample of oil may be determinded from the amount of phosphorus present, the factor usually used, being $P_2O_5 \times 11{\cdot}37 =$ lecithin; where this method is used allowance must be made for the amount of phosphorus present as mineral phosphates (cf. E. Boedtker, *J.S.C.I.*, 1925, 44, B728). Maize oil contains by far the largest amount of lecithin of any of the seed oils, well over one per cent. being usually present—an equally large, or possibly larger proportion, is contained in bone marrow. For synthetic lecithin see Levene and Rolf, *J.S.C.I.*, 1924, 43, B888.

Waxes differ from fats in that in the former the glycerol of the fats is replaced by monohydric alcohols of high molecular weight, thus spermaceti contains cetyl alcohol, $C_{16}H_{33}{\cdot}OH$, and beeswax contains melissyl alcohol, $C_{30}H_{61}{\cdot}OH$. Dihydric alcohols occasionally occur in small quantities in some waxes. Alcohols of high molecular weight also exist in small quantities in fats. Cholesterol, $C_{27}H_{46}O$ occurs free in all animal fats, whilst phytosterols of somewhat varying composition occur in vegetable oils. The difference in the melting-points of these two substances and particularly in those of their acetates is the basis of a means of the differentiation of animal and vegetable oils. The properties of the sterols and their salts are given on page 40; details of the phytosteryl acetate method are given on page 124.

CHAPTER IV

PROPERTIES OF INDIVIDUAL GLYCERIDES, ACIDS AND ALCOHOLS

1. Glycerides

The glycerides present in oils and fats, at least before rancidity sets in, are almost entirely triglycerides, so that the mono and diglycerides known have nearly all been obtained by synthetic methods. The α mono-glycerides are somewhat readily synthesised by heating monochlor-hydrin with the sodium salt of the fatty acid in question, whilst the β monoglycerides have been prepared by using dichlorhydrin and removing chloro derivatives by the action of silver nitrite.

The diglycerides are prepared by heating one molecule of dichlorhydrin and two molecules of the sodium salt of the fatty acid concerned. The diglycerides can exist, as explained above, in two forms, the symmetrical and the unsymmetrical.

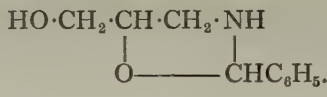
The simple triglycerides may be prepared by heating together the sodium

Table IV.—Properties of Triglycerides

Triglyceride.	Formula.	Molecular Weight.	Specific Gravity.	B.P. °C.	M.P. °C.
Triformin . .	$C_3H_5(H{\cdot}CO{\cdot}O)_3$	176	$1{\cdot}3200/18$	266	18
Triacetin . .	$C_3H_5(CH_3{\cdot}CO{\cdot}O)_3$	218	$1{\cdot}1603/15$	258	..
Tributyrin . .	$C_3H_5(C_3H_7{\cdot}CO{\cdot}O)_3$	302	$1{\cdot}0324/\frac{20}{4}$	287	..
Trivalerin . .	$C_3H_5(C_4H_9{\cdot}CO{\cdot}O)_3$	344	..	..	..
Tricaproin . .	$C_3H_5(C_5H_{11}{\cdot}CO{\cdot}O)_3$	386	$\cdot9817/\frac{20}{4}$	..	−25
Tricaprylin .	$C_3H_5(C_7H_{15}{\cdot}CO{\cdot}O)_3$	470	$\cdot9540/\frac{20}{4}$	..	8
Tricaprin . .	$C_3H_5(C_9H_{19}{\cdot}CO{\cdot}O)_3$	554	$\cdot9205/\frac{40}{4}$	..	31
Trilaurin . .	$C_3H_5(C_{11}H_{23}{\cdot}CO{\cdot}O)_3$	638	$\cdot8944/\frac{60}{4}$	..	45
Trimyristin. .	$C_3H_5(C_{13}H_{27}{\cdot}CO{\cdot}O)_3$	722	$\cdot8848/\frac{60}{4}$	..	56
Tripalmitin. .	$C_3H_5(C_{15}H_{31}{\cdot}CO{\cdot}O)_3$	806	$\cdot8657/\frac{80}{4}$	..	63
Tristearin . .	$C_3H_5(C_{17}H_{35}{\cdot}CO{\cdot}O)_3$	890	$\cdot8621/\frac{80}{4}$	..	71·6
Triarachin . .	$C_3H_5(C_{19}H_{39}{\cdot}CO{\cdot}O)_3$	974	..	..	..
Tricerotin . .	$C_3H_5(C_{25}H_{51}{\cdot}CO{\cdot}O)_3$	1226	..	..	77
Trimelissin .	$C_3H_5(C_{29}H_{59}{\cdot}CO{\cdot}O)_3$	1394	..	..	89
Triolein . .	$C_3H_5(C_{17}H_{33}{\cdot}CO{\cdot}O)_3$	884	$\cdot900/15$	..	S.P. −4
Trierucin . .	$C_3H_5(C_{21}H_{41}{\cdot}CO{\cdot}O)_3$	1052	..	..	31
Triricinolein .	$C_3H_5(C_{17}H_{32}{\cdot}OH{\cdot}CO{\cdot}O)_3$	932	$\cdot959/15$	..	..
Trilinolein . .	$C_3H_5(C_{17}H_{31}{\cdot}CO{\cdot}O)_3$	878	..	..	..
Trilinolenin .	$C_3H_5(C_{17}H_{29}{\cdot}CO{\cdot}O)_3$	872	..	..	..
Triclupanodonin	$C_3H_5(C_{17}H_{27}{\cdot}CO{\cdot}O)_3$	866	..	..	..

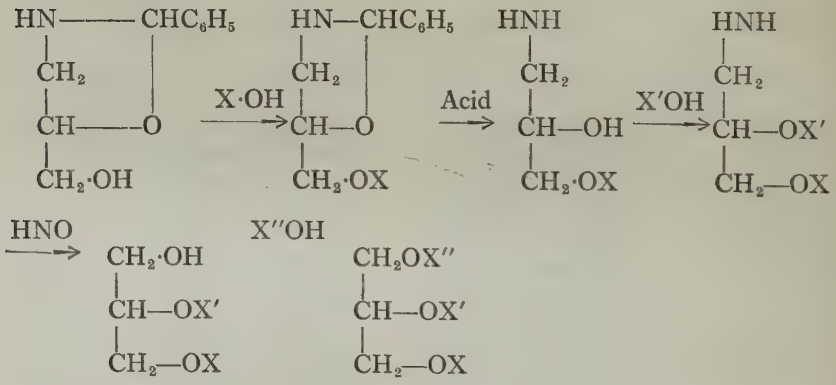
salts of the fatty acids with tribromhydrin. Those that have been isolated or prepared synthetically are arranged in a table above, together with their properties.

It has been explained above that natural oils contain very few simple triglycerides, and that the bulk of them is composed of mixed triglycerides of various kinds. A number of such compounds have been isolated from various fats, whilst others have been prepared synthetically by various processes. It is by no means easy to fix definitely the structure of such mixed glycerides, and even the use of acetone glycerol for their synthesis, as suggested by Fischer, is not always successful, as the molecules frequently rearrange themselves owing to wandering of the fatty acid radicle and thus uncertainty is introduced. Bergmann has lately introduced the substance 2-phenyl-5-hydroxymethyloxazolidine as reported by E. F. Armstrong and Allan (*J.S.C.I.*, 1924, 43, 209T).



This has but one alcohol group available for glyceride formation so that the monoglyceride will readily be formed. This compound when formed can be hydrolysed to benzaldehyde and aminopropyleneglycol, when a further fatty acid radicle may be introduced and, finally, the use of nitrous acid will decompose this last compound with liberation of a third hydroxy group from which the triglyceride of known structure can readily be prepared.

The nature of these reactions is shown in the following series of formulæ :



Further work on somewhat similar lines has been carried out by Irvine for the Food Investigation Board (*F.I.B.*, 1923, 6, 8, 65).

The properties of a number of mixed triglycerides are given in the table below. The structure assigned to these by the workers who have prepared them (mostly Grun and his co-workers) is given in each case although there is still considerable doubt about many of them. It is most desirable that all those glycerides likely to be found in natural fats should be prepared by some such method as that of Bergmann (v.s.) and their properties carefully studied so that it will be possible to determine with certainty the constitution of those isolated from natural sources.

TABLE V.—PROPERTIES OF MIXED TRIGLYCERIDES

Mixed Triglycerides.	M. Pt. °C.	B. Pt. @ Pressure. °C.	Other Properties.
α–Aceto–*β*–*γ*–diformin		157 @ 27 mm.	
β–Aceto–*α*–*γ*–dibutyrin		289–290 @ 760 mm.	$n_D^{40} = 1{\cdot}4262$
β–Aceto–*α*–*γ*–dilaurin			
β–Aceto–*α*–*γ*–dimyristin	41·5–46·5		
α–Aceto–*β*–*γ*–dipalmitin	67		
β–Aceto–*α*–*γ*–dipalmitin	49		solidified @ 29
α–Aceto–*β*–*γ*–distearin	44		
β–Aceto–*α*–*γ*–distearin	56·5		
β–Lauro–*α*–*γ*–dimyristin	46·5		
α–Lauro–*β*–*γ*–dimyristin	45		
α–Myristo–*β*–*γ*–dilaurin	41		
β–Myristo–*α*–*γ*–dilaurin	32		
α–Stearo–*β*–*γ*–dilaurin	46		
β–Stearo–*α*–*γ*–dilaurin	37·5		
α–Lauro–*β*–*γ*–distearin	52·5		
β–Lauro–*α*–*γ*–distearin	53·5 and 68·5		
α–Lauro–*β*–stearo–*γ*–myristin	37–38		
α–Stearo–*β*–myristo–*γ*–laurin	48–49		
α–Stearo–*β*–lauro–*γ*–myristin	42		
α–Myristo–*β*–*γ*–distearin	52 and 62		
β–Myristo–*α*–*γ*–distearin	57 and 58·8		
α–Palmito–*β*–*γ*–distearin	63		n 1·4396
β–Palmito–*α*–*γ*–distearin	52·2 and 62		
α–Stearo–*β*–*γ*–dipalmitin	60		n_D 1·4430
β–Stearo–*α*–*γ*–dipalmitin	60		n_D 1·4407
Stearodipalmitin	55		

2. ACIDS

The larger proportion by far of the acids contained in fats are those having a straight carbon chain either saturated or more or less unsaturated. A few having a ring formation are known and are of some importance, but they occur mostly in the lesser known fats. The properties of the various acids which have been isolated are given below together with those of their important compounds. For the synthesis of fatty acids from paraffins see Marcusson, *J.S.C.I.*, 1925, 44, B250. For an X-ray examination cf. *J.C.S.*, 1924, 125, 2622. The commercial distillation of fatty acids and wool grease has been described by G. F. Pickering (*J.S.C.I.*, 1925, 44, 424T).

ACIDS WITH THE GENERAL FORMULA, $C_nH_{2n}O_2$

With the exception of daturic, valeric acid and the possible exception of acetic acids, which are said to occur naturally in one or two fats, the acids

naturally present in fats have always an even number of carbon atoms. It is quite possible that underlying this fact some important principles will be discovered, but up to the present time no really serious endeavours have been made to explain it and a large amount of experimental evidence will be required before it can be attempted with any certainty.

Acetic Acid. $CH_3 \cdot COOH$

This acid is said to occur in the oil of *argemone mexicana* (Bhaduri, *J.S.C.I.*, 1914, 33, 266), in the oil of the Proso millet, *Panicum miliacum* (Dunbar and Binnewies, *J.S.C.I.*, 1920, 39, 346A), and in cocao butter (Knapp, *J.S.C.I.*, 1923, 42, 508A), but there is still possibly a little doubt as to whether the acid does occur naturally in oils and fats. A method for the separation of this acid from propionic and butyric acids has been suggested by Crowell (*Analyst*, 1918, 43, 172). Cf. page 58.

Butyric Acid. $CH_3 \cdot (CH_2)_2 \cdot COOH$

Occurs in the milk fat of the cow, sheep, goat, etc. It is absent, or nearly so, from human milk fat. When pure it is a colourless liquid with an odour resembling acetic acid; the odour of its aqueous solution recalls that of rancid butter. Sol.Pt.—19°. M.Pt.—7°. B.Pt. 163°. $d\frac{20}{4}$, 0·959. n_D^{20}, 1·3991. It is miscible in all proportions with water, alcohol or ether, but much less soluble in salt solution $_4$ it is freely volatile with steam.

A qualitative test for butyric acid has been proposed by Denigès (*Analyst*, 1918, 43, 145), but Bamford (*ibid.*, 1924, 49, 226) has found that this test is not reliable. Moderate quantities may be detected in fats by the smell of ethyl butyrate formed when the fat is treated with dilute alcoholic potash containing insufficient potash to produce complete saponification. Under these circumstances, in the presence of butyric acid, ethyl butyrate will be formed, which may be recognised by its odour.

The salts of butyric acid formed with the alkali metals are soluble in water as indeed are the alkali salts of all the fatty acids. The other salts that have been studied are given below.

Ammonium butyrate (Falciola, *Analyst*, 1911, 36, 114).—A deliquescent salt. M.Pt. 70°–85°. Very soluble in methyl or in ethyl alcohol or in chloroform. Nearly insoluble in ether, acetone or benzene.

Barium butyrate.—$Ba(C_4H_7O_2)_2 \cdot 4H_2O$. The anhydrous salt is soluble in water at 15°, 38, slightly less, down to 35, at 100°; it is soluble in absolute alcohol 0·13 and in 97 per cent. alcohol 0·17, at ordinary temperatures. (Crowell, *J. Amer. C.S.*, 1918, 40, 453).

Calcium butyrate.—$Ca(C_4H_7O_2)_2 \cdot H_2O$. The anhydrous salt is soluble in water at 15°, 29, but this solubility decreases with rise in temperature and the salt is nearly insoluble in boiling water. Soluble in alcohol.

Quinine butyrate (Phelps and Palmer, *J.S.C.I.*, 1917, 36, 567).—M.Pt. 77·5° (Uncorr.). Soluble in chloroform 4.

Silver butyrate.—$AgC_4H_7O_2$. The solubility in water is 0·49, but this is considerably reduced where excess of silver salt is present—thus Jensen found that in N/20 silver nitrate solution the solubility was 0·35.

Methyl butyrate.—d_4, 0·920. B.Pt., 102° @ 760 mm.

Ethyl butyrate.—Sol.Pt.—80°. d_4, 0·900. B.Pt.,120° @ 760 mm. n_D^{20}, 1·4000.

Derivatives.—*Butyric anhydride*. B.Pt. 192°. *Butyric Amide*. M.Pt. 115°. *Butyric toluidide*. M.Pt. 74°. *Butyric naphthalide*. M.Pt. 120°.

Valeric Acid. $CH_3(CH_2)_3 \cdot COOH$

The occurrence of valeric acid in the natural state in fats is open to question. Its presence in various oils such as dolphin oil, has been reported, but the possibility of this being a mixture of butyric and caproic acid is quite a strong one and the matter requires to be reinvestigated, although E. André (*Analyst*, 1924, 49, 533) considers that it is undoubtedly isopropylacetic acid. The normal acid is a colourless liquid having an unpleasant rancid odour more pronounced than that of butyric acid. Sol.Pt., −19°; B.Pt., 186°. d_4, 0·958. Soluble in water 3·3.

Methyl valerate.—d = 0·910. B.Pt. 127°.

Ethyl valerate.—d = 0·894. B.Pt. 145°.

Caproic Acid. $CH_3(CH_2)_4 \cdot COOH$

Caproic acid occurs in several fats, the best known of which are butter fat and coconut oil. It is probably present also in palm-kernel oil and other oils of the same nature; its presence in the oil of the seeds of the evening primrose (*Oenothera biennis*) has also been reported (*J.S.C.I.*, 1919, 38, 426A). Colourless liquid having an odour of sweat. M.Pt., −8°. B.Pt., 202°. d_4^{20}, 0·924., n_D^{20}, 1·4164. Solubility in water 0·9. Volatile in steam.

Barium caproate.—$Ba(C_6H_{11}O_2)_2 \cdot 2H_2O$. Soluble in water 11.

Calcium caproate.—$Ca(C_6H_{11}O_2)_2 \cdot H_2O$. Soluble in water 4·5.

Lead caproate.—M.Pt. 73°–74°; sol. in ether, 1·36 at B.Pt. and in petroleum ether (40°–60°) 0·06 at B.Pt.

Silver caproate.—Soluble in water, 0·089, in N/20 $AgNO_3$, 0·029.

Strontium caproate.—This salt is 11 times as soluble in water as strontium caprylate.

Zinc caproate.—Zn $(C_6H_{11}O_2)_2 \cdot H_2O$. The anhydrous salt is soluble in water 1 at 35°.

Methyl caproate.—d_4, 0·931. B.Pt. 150° at 760 mm. 52° at 15 mm.

Ethyl caproate.—d_4, 0·889. B.Pt. 167° at 760 mm.

Derivatives.—*Caproic anhydride.* B.Pt. 242°. *Caproic amide.* M.Pt. 100°. *Caproic toluidide.* M.Pt. 75°. *Caproic naphthalide.* M.Pt. 112°.

Caprylic Acid. $CH_3(CH_2)_6 \cdot COOH$

This acid occurs in butter fat, in coconut oil and other oils of the same family such as palm kernel. At ordinary temperatures it is a colourless liquid, having an odour of sweat and resembling caproic acid. Readily volatile in steam. Sol. Pt., 12°. M.Pt., 16·5°. B.Pt. 236° at 760; 124° at 10 mm. d_4, 0·927, n_D^{20}, 1·4283. Soluble in water 0·08 at 15°; 0·25 at 100°.

Ammonium caprylate.—$NH_4C_8H_{15}O_2$ (Falciola, *Analyst*, 1911, 36, 114). M.Pt. 70°–85°. Gives a turbid solution in water. May be recrystallised from benzene. Soluble in methyl or ethyl alcohols or in chloroform. Sparingly soluble in ether, carbon bisulphide and chloroform.

Barium caprylate.—$Ba(C_8H_{15}O_2)_2$. Soluble in water 0·61

Cadmium caprylate.—Soluble in water about 0·1.

Copper caprylate.—$Cu(C_8H_{15}O_2)_2$. Crystallises from alcohol. M.Pt. 265°.

Lead caprylate.—M.Pt. 83·5°–84·5°. Soluble in ether 0·09 at 20°, 0·55 at the B.Pt. Practically insoluble in petroleum ether (40°–60°) at 20°—soluble 0·04 at the B.Pt.

Silver caprylate.—Soluble in water 0·018, in N/10 $AgNO_3$ 0·005.

Strontium caprylate.—This salt has only one-eleventh the solubility in water of strontium caproate (Gsell, *Analyst*, 1907, 32, 95).

Methyl caprylate.—d_4, 0·894. Sol. Pt. −40°. B.Pt. 193° at 760 mm., 95° at 25 mm., and 83° at 15 mm.

Ethyl caprylate.—d_4, 0·884. Sol. Pt. −47°. B.Pt. 207°–208°.

Derivatives.—Caprylic anhydride. B.Pt. 280°–290° (cf. *J.S.C.I.*, 1925, 44, B680). *Caprylic amide.* M.Pt. 97°–98°. *Caprylic anilide.* M.Pt. 57°. *Caprylic toluidide.* M.Pt. 67°. *Caprylic naphthalide.* M.Pt. 95°.

Capric Acid. $CH_3(CH_2)_8 \cdot COOH$

Capric acid occurs in butter fat, to a small extent in coconut and palm-kernel oils and, it is stated, in coffee-berry oil. Pavlenko states that the fatty acids of elm-seed oil contain approximately 50 per cent. of this acid; the statement needs confirming. The acid is a white crystalline solid, having an odour similar to that of the lower members of the series but less pronounced. M.Pt. 31·3°; B.Pt. 268°–270° at 760 mm., 200° at 100 mm., and 153°–154° at 13 mm. d_4^{40}, 0·886; n_D^{40}, 1·4286. It is practically insoluble in water at ordinary temperatures, soluble about 0·1 at 100°.

The barium, calcium and strontium salts of capric acid are very slightly soluble in hot water and are practically insoluble in cold water, but they are soluble to a certain extent in boiling alcohol.

Lead caprate.—M.Pt. 100°. Soluble in ether 0·03 at 20°, 0·43 at the B.Pt. Practically insoluble in petroleum ether (40°–60°) at 20°, soluble 0·017 at the B.Pt.

Methyl caprate.—Sol. Pt. −18°. B.Pt. 223° at 760 mm., 114 at 15 mm.

Ethyl caprate.—d_0, 0·862. B.Pt. 242°–245° at 760 mm.

Derivatives.—Capric amide. M.Pt. 108°. *Capric anilide.* M.Pt. 61°. *Capric toluidide.* M.Pt. 80°. *Capric naphthalide.* M.Pt. 99°. *Capric anhydride.* M.Pt. 23·9°; Sp. Gr. 0·8596 at 70°/4°; n_D^{70}, 1·4234 (*J.S.C.I.*, 1925, 44, B680).

Lauric Acid. $CH_3(CH_2)_{10} \cdot COOH$

Kusu fat and tangkallak fat are composed very largely of the glycerides of lauric acid whilst notable quantities of this acid are contained in coconut and palm-kernel oils and in laurel-oil and other similar oils. A white solid having little odour. M.Pt. 43·6°. B.Pt. at 760 mm., with slight decomposition, about 300°, 225° at 100 mm., and 176° at 15 mm. d_4^{20}, 0·883, d_4^{60}, 0·864, n_D^{60}, 1·4267. Insoluble in cold water, very slightly soluble in boiling water. Somewhat volatile in steam.

Ammonium laurate (Falciola, *Analyst*, 1911, 36, 114). M.Pt. about 75°. Insoluble in cold water. Soluble 4·8 in absolute alcohol at 7°, whilst in ammoniacal alcohol it is soluble 3·5. Soluble in methyl alcohol and hot benzene (from which it crystallises) and sparingly soluble in ether and acetone.

Barium laurate.—$BaLa_2$. Soluble in water 0·008 at 15·3°, 0·011 at 50°. Soluble in ethyl alcohol 0·010 at 16·5°, 0·010 at 25°, 0·013 at 35°, 0·007 at 50°. Soluble in methyl alcohol 0·084 at 15°, 0·096 at 25°, 0·121 at 35°, 0·163 at 50·5°. Soluble in ether 0·007 at 25°. Soluble in amyl alcohol 0·009 at 25° (Jacobson and Holmes, *J.S.C.I.*, 1916, 35, 696. Practically all the solubility data following are by the same authors).

Beryllium laurate.—The salt produced by precipitation of ammonium laurate with the calculated proportion of beryllium nitrate is the basic salt having the composition Be(OH)La, it is soluble in ethyl alcohol 0·004, in methyl alcohol 0·050.

Calcium laurate.—$Ca\overline{La}_2 \cdot H_2O$. Soluble in water 0·004 at 15°, 0·055 at 100°. Soluble in alcohol 0·072 at 15°, 2·20 at 78°.

Cobalt laurate.—$Co\overline{La}_2 \cdot H_2O$. Soluble in water 0·007 at 15°, ·038 at 100°. Soluble in alcohol 0·017 at 15°, 1·80 at 78°.

Copper laurate.—$Cu\overline{La}_2$. Soluble in water 0·002 at 15°, 0·003 at 100°. Soluble in alcohol 0·078 at 15°, 0·65 at 78°.

Ferric laurate.—$Fe_3\overline{La}_6(OH)_3$ (*J.C.S.*, 1916, 110, i, 314). Soluble in chloroform and benzene.

Lead laurate.—$Pb\overline{La}_2$. M.Pt. 104·7° (Jacobson and Holmes). 103°–104° (Neave). Soluble in water 0·008. Soluble in alcohol 0·009 at 25°, 0·032 at 35°, 0·264 at 50°. Soluble in methyl alcohol 0·061 at 15·5°, 0·096 at 25°, 0·113 at 35°, 0·280 at 50°. Soluble in ether 0·010 at 14·5°, 0·021 at 35°. Practically insoluble in boiling petroleum ether.

Lithium laurate.—$Li\overline{La}$. M.Pt. 229·2°–229·8°. Soluble in water 0·154 at 16·3°, 0·187 at 25°, 0·207 at 35°, 0·280 at 50°. Soluble in ethyl alcohol 0·403 at 20°, 0·447 at 25·4°, 0·546 at 35°, 0·782 at 50°, 1·149 at 65°. Soluble in methyl alcohol 3·16 at 15·2°, 3·77 at 25°, 4·60 at 34·6°, 6·09 at 50°. Soluble in ether 0·011 at 15·8°, 0·006 at 25°. Soluble in amyl alcohol 0·073 at 16°, 0·111 at 25·7°, 0·126 at 35°, 0·203 at 49·2°. Soluble in chloroform 0·006 at 15·2°. Soluble in amyl acetate 0·068 at 14·5°, 0·064 at 25°, 0·061 at 35° and 50°. Soluble in methyl acetate 0·026 at 24·5°. Soluble in acetone 0·300 at 15°, 0·376 at 25°, 0·430 at 35°.

Magnesium laurate.—$Mg\overline{La}(2H_2O)$. M.Pt. anhydrous salt 150·4°. The anhydrous salt is soluble in water 0·010 at 15°, 0·010 at 35°, 0·026 at 50°, 0·041 at 100°. Soluble in ethyl alcohol 0·519 at 15°, 0·591 at 25°, 0·805 at 35°, 1·267 at 50°. Oudemans states that the hydrated salt is soluble in methyl alcohol 1·1 at 15° and 25°. In ether 0·015 at 25°; in ethyl acetate 0·004 at 15°, 0·011 at 35°, 0·024 at 50°; in acetone 0·117 at 15°, 0·123 at 25°; in amyl alcohol 0·191 at 15°, 0·236 at 25°, 1·481 at 35°, 4·869 at 50°; in amyl acetate 0·119 at 15°, 0·162 at 25°, 0·259 at 34·6°, 1·939 at 50°.

Manganese laurate.—$Mn\overline{La}$. Soluble in water 0·001 at 15°, 0·040 at 100°. Soluble in alcohol 0·048 at 15°, 0·38 at 78°.

Nickel laurate.—$Ni\overline{La} \cdot H_2O$(or $3H_2O$). Soluble in water 0·020 at 15°, 0·039 at 100°. Soluble in alcohol 0·064 at 15°, 0·668 at 78°.

Silver laurate.—$Ag\overline{La}$. Insoluble in water at 15° and practically insoluble in ethyl alcohol (although Oudemans gives the solubility in alcohol as about 0·03) and ether. Soluble in methyl alcohol 0·074 at 15°, 0·083 at 50°.

Strontium laurate.—$Sr\overline{La}_2 \cdot H_2O$. Soluble in water 0·027 at 15°, 0·036 at 100°. Soluble in alcohol 0·96 at 15°, 0·36 at 78°.

Zinc laurate.—$Zn\overline{La}_2$. Soluble in water 0·01 at 15°, 0·019 at 100°. Soluble in alcohol 0·013 at 15°, 0·88 at 78°.

Methyl laurate.—M.Pt. 5°. B.Pt. 141° at 15 mm., 148° at 18 mm.

Ethyl laurate.—Sol. Pt. —10°. B.Pt. 269° at 760 mm.

Derivatives.—Lauric anhydride. M.Pt. 42° (cf. *J.S.C.I.*, 1925, 44, B680). *Lauric amide.* M.Pt. 110°. *Lauric anilide.* M.Pt. 68°. *Lauric toluidide.* M.Pt. 81°–82°. *Lauric naphthalide.* M.Pt. 100°.

Myristic Acid. $CH_3(CH_2)_{12} \cdot COOH$

Myristic acid constitutes the bulk of the fatty acids of nutmeg butter, " Birola butter " and " Ochoco fat " and is also contained in considerable quantities in many of the solid and liquid fats. M.Pt. 53·8°. B.Pt. 250·5°

at 100 mm., 196·5° at 15 mm. d_4^{60}, 0·858, n_D^{60}, 1·4308°. Insoluble in boiling water. Slightly soluble in alcohol and ether in the cold, easily soluble in either of the boiling solvents.

Ammonium myristate.—$NH_4\overline{My}$. M.Pt. 75° (imperfectly). Practically insoluble in cold ether or chloroform, sparingly soluble in cold water, acetone or methyl alcohol, somewhat more soluble in alcohol.

Beryllium myristate.—$Be(OH)\overline{My}$. Soluble in water at 25°, 0·004, in methyl alcohol at 25°, 0·047.

Barium myristate.—$Ba\overline{My}_2$. Soluble in water 0·007 at 15·3°, 0·01 at 50°. Soluble in ethyl alcohol 0·009 at 16·5°, 0·011 at 25°, 0·013 at 35°, 0·004 at 50°. Soluble in methyl alcohol 0·057 at 15°, 0·070 at 25°, 0·087 at 35°, 0·108 at 50·5°. Soluble in ether 0·003 at 25°. Soluble in amyl alcohol 0·009 at 25°.

Lead myristate.—$Pb\overline{My}_2$. Soluble in water 0·005 at 35°, 0·006 at 50°. Soluble in ethyl alcohol 0·004 at 25°, 0·004 at 35°, 0·052 at 50°. Soluble in methyl alcohol 0·056 at 15·5°, 0·078 at 25°, 0·082 at 35°, 0·019 at 50°. Soluble in ethyl acetate 0·010 at 14°, 0·015 at 35·5°, 0·077 at 50°. Soluble in benzene 0·010 at 15°. Soluble in ether 0·013 at 14·5°, 0·056 at 36°. Soluble in petroleum ether (40°–60°) 0·021 at 40°.

Lithium myristate.—$Li\overline{My}$. M.Pt. 223·6°–224·2°. Soluble in water 0·027 at 16·3°, 0·036 at 25°, 0·042 at 35°, 0·062 at 50°. Soluble in ethyl alcohol 0·194 at 20°, 0·224 at 25·4°, 0·278 at 35°, 0·435 at 50°, 0·669 at 65°. Soluble in methyl alcohol 1·346 at 15·2°, 1·680 at 25°, 2·193 at 34·6°, 3·281 at 50. Soluble in ether 0·013 at 15·8°, 0·004 at 25°. Soluble in amyl alcohol 0·029 at 16°, 0·046 at 25·7°, 0·062 at 35°, 0·109 at 49·2°. Soluble in chloroform 0·004 at 15·2°. Soluble in amyl acetate 0·037 at 14·5°, 0·034 at 25°, 0·044 at 35°, 0·045 at 50°. Soluble in methyl acetate 0·013 at 24·5°. Soluble in acetone 0·413 at 15°, 0·447 at 25°, 0·502 at 35°.

Magnesium myristate.—$Mg\overline{My}$. M.Pt. 131·6°. Soluble in water 0·006 at 15° and 25°, 0·007 at 35°, 0·014 at 50°. Soluble in ethyl alcohol 0·158 at 15°, 0·236 at 25°, 0·373 at 35°, 0·577 at 50°. Soluble in methyl alcohol 0·571 at 15°, 0·763 at 25°. Soluble in ether 0·010 at 25°. Soluble in ethyl acetate 0·004 at 15°, 0·010 at 35°, 0·021 at 50° Soluble in acetone 0·142 at 15°, 0·145 at 25°. Soluble in amyl alcohol 0·086 at 15°, 0·145 at 25°, 0·438 at 35°, 1·893 at 50°. Soluble in amyl acetate 0·063 at 15°, 0·073 at 25°, 0·105 at 34·6°, 0·605 at 50°.

Silver myristate.—$Ag\overline{My}$. M.Pt. 211°. Soluble in water 0·007 at 35° and 50°. Soluble in ethyl alcohol 0·008 at 25° and 50°.

Methyl myristate.—M.Pt. 18°. B.Pt. 296° at 760 mm. 167°–168° at 15 mm.

Ethyl ester.—Sol. Pt. 10·5°–11·5°. B.Pt. 295° at 760 mm.

Derivatives.—*Myristic anhydride.* M.Pt. 51·5° (cf. *J.S.C.I.*, 1925, 44, B680). *Myristic amide.* M.Pt. 102°. *Myristic toluidide.* M.Pt. 93°. *Myristic naphthalide.* M.Pt. 105°.

Palmitic Acid. $CH_3(CH_2)_{14}\cdot COOH$

Palmitic acid is one of the commoner constituents of fats particularly of the solid fats and is an important constituent of palm-oil. M.Pt. 62·6°. B.Pt. 271·5° at 100 mm. 215° at 15 mm. d_4^{80}, 0·841, n_D^{60}, 1·4324, n_D^{70}, 1·4298. It is insoluble in either cold or boiling water. The solubility in alcohol of various strengths has been studied by various workers, the results obtained by Falciola (*Analyst*, 1911, 36, 23) are given in the following table :

TABLE VI.—SOLUBILITY OF PALMITIC ACID IN ALCOHOL

Temp.	Solubility in grams per 100 c.c. in		
	Abs. Alc.	75 % Alc.	50 %. Alc.
40°	31·9	3·6	0·3
30°	..	1·2	0·12
20°	9·2	0·4	0·09
10°	2·8	0·2	0·05

The results obtained by other workers are of the same order (cf. Hehner and Mitchell, *Analyst*, 1896, 21, 323).

Twitchell (*Analyst*, 1914, 39, 448, cf. Meldrum, *ibid.*, 1913, 38, 579) has determined the M.Pts. of mixtures of palmitic acid with stearic, behenic and oleic acids and his results are as follows : Melting-points were determined by a modification of the capillary-tube method, under somewhat rigid conditions, and Heintz's observation confirmed that the depression of the melting-point is proportional to the amount of the second acid and substantially independent of its nature. For example, a nearly pure stearic acid had a m.pt. of 69·30° C.; a mixture of 9 parts of this acid with 1 part of palmitic, oleic, or behenic acid melted at 67·25° C. (depression 2·05°); and a mixture of eight parts of stearic acid with 2 of palmitic, oleic, or behenic acid, or 1 of oleic and 1 of palmitic acid melted at 65·25° C. (depression 4·05°). Similarly the m.pt. of palmitic acid (62·44) was depressed 2·05° by mixing with one-ninth of its weight of stearic, oleic or behenic acid, and 4·16° by mixing with one-quarter of its weight of these acids. The m.pt. of behenic acid (79·99°) was depressed 4·33° when 2 parts of stearic palmitic or oleic acid were added to 8 parts of behenic acid. In the analysis of mixtures of fatty acids the above data are used as follows : 20 parts of the mixture are added to 80 parts of palmitic, stearic, behenic, etc., acids, and the melting-point of the mixture determined. For example, 20 parts of cotton-seed oil fatty acids with 80 of palmitic acid give a mixture melting at 59·26°. This is a depression of 3·18° and corresponds to a mixture of 84·6 parts palmitic acid with 15·4 parts other acids. The 20 parts of cotton-seed oil fatty acids therefore contain 4·6 parts palmitic acid, or 23 per cent.

Eisenstein (*J.S.C.I.*, 1920, 39, 663A) has determined the M.Pts. of mixtures with stearic acid and he finds that " the melting-point curve of mixtures of palmitic acid and stearic acid has portions which are nearly straight lines between 70 and 100 per cent. of palmitic acid and 60 and 100 per cent. of stearic acid.

Carlinfanti and Levi-Malvano (*Analyst*, 1910, 35, 30) determined the Sol. Pts. of mixtures of palmitic, stearic and oleic acids, and found the following values.

The authors conclude that mixtures of stearic and palmitic acids form four series of solid solutions, and one addition compound, which would correspond to the old margaric acid, to the more recent daturic acid, and possibly to the synthetical margaric acid of Heintz and Krafft. The mixtures of stearic acid with oleic acid, and of palmitic acid with oleic acid, however, form only a single series of solid solutions.

TABLE VII.—SOLIDIFICATION POINTS OF MIXTURES OF PALMITIC, STEARIC AND OLEIC ACIDS

Stearic Acid.	Palmitic Acid.	Beginning of Crystallisation.	Stearic Acid.	Oleic Acid.	Beginning of Crystallisation.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.
100	0	68·2	0	100	9·00	100	0	61.00
90	10	65·90	5	95	23·45	90	10	59·20
—	—	(end 61·5)	15	85	34·25	80	20	57·30
80	20	63·5	25	75	46·60	70	30	55·10
70	30	60·80	35	65	51·90	60	40	52·60
—	—	(end 57·0)	..	..	(end 34)	..	..	(end 44)
60	40	57·65	46	54	55·95	50	50	49·75
52·5	47·5	56·00	55	45	58·65	40	60	46·25
—	—	(end 56·0)	..	..	(end 45)	30	70	41·60
50	50	56·25	65	35	61·25	20	80	35·00
40	60	55·90	75	25	63·40	10	90	24·80
30	70	54·75	..	..	(end 57)	0	100	9·00
—	—	(end 54·79)	85	15	65·40	..	..	..
20	80	55·75	95	5	67·15	..	..	..
10	90	58·40	100	0	68·20	..	..	..
5	95	59·60	..	..	..	..	..	..
1	100	61·00	..	..	..	..	..	..

The results obtained with mixtures of all three acids grouped in different systems were as follows:

TABLE VIII.—SOLIDIFICATION POINTS OF MIXTURES OF STEARIC, PALMITIC AND OLEIC ACIDS

Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.	Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.	°C.
74·5	13	12·5	62·30	91·5	7·5	1	65·60
66	17	17	60·15	80	17·5	2·5	63·00
61	19·5	19·5	58·80	69	27·5	3·5	60·10
51	24·5	24·5	55·60	57	38	5	56·30
29	35·5	35·5	48·65	46	48	6	54·60
12	44	44	45·15	34·5	58·5	7	53·80
				27·5	64	8·5	52·70
80	3	17	64·10	23·5	68·5	8·5	52·70
74	4	22	62·80	12	78·5	9·5	55·05
69	4·5	26·5	61·65	40·5	55	4·5	54·80
63·5	5·5	31	60·40				
57·5	6·5	36	58·65	58·5	19·5	22	58·10
51·5	7·5	41	56·90	47	31	22	53·70
46	8	46	55·10	41	36·5	22·5	52·00
41	7·5	51·5	53·30	39	39	22	51·65

TABLE VIII.—*Continued.*

Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.	Stearic Acid.	Palmitic Acid.	Oleic Acid.	Beginning of Crystallisation.
Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.	°C.
35	43	22	51·65	16·5	37·5	46	44·70
31	47	22	51·30	5·5	48·5	46	47·30
27·5	50·5	22	50·90				
24	54	22	50·30	24·5	8	67·5	44·95
19·5	58·5	22	50·10	19·5	12·5	68	40·85
15·5	62	22·5	50·70	14·5	18	67·5	38·20
8	70	22	53·30	10	22·5	67·5	36·90
				3·5	29	67·5	38·85
40·5	13·5	46	52·55				
32·5	21·5	46	48·20	5·5	77·5	19·5	54·85
29	25	46	46·50	8	66	26	52·40
27	26·5	46	46·10	20	30·5	49·5	44·55
21·5	32	46·5	45·40				

Pascal (*J.S.C.I.*, 1914, 33, 602) determined the refractive indices of mixtures of palmitic, stearic and oleic acids, and obtained a series of figures which may be found in the original paper (*Bull. Soc. Chim.*, 1914, 15, 360, 367).

An isopalmitic acid has been said to be contained in "chrysalis oil" (Kawase, etc., *J.S.C.I.*, 1921, 40, 664A). This is said to crystallise in flat prisms from alcohol, and have M.Pt. 57°–59°. The acid and its magnesium salt were found to be less soluble in alcohol than is palmitic acid, and methyl isopalmitate was found to have M.Pt. 38°.

Ammonium palmitate.—Falciola (*Analyst*, 1911, 36, 23) found the solubility in alcohol to be as follows:

Temp. °C.	Abs. Alc.	75 per cent. Alc.	50 per cent. Alc.
50	11·0	..	..
40	4·5	14·8	6·7
30	..	11·0	..
20	1·4	4·3	5·3
10	0·7	1·8	..

It is soluble in ether 0·29, and in acetone 0·20 both at 13°.

Barium palmitate.—Soluble in water 0·004 at 15°, 0·007 at 50°. Soluble in alcohol 0·01 at 16·5°. Soluble in methyl alcohol 0·045 at 15°, 0·088 at 50·5°. Soluble in ether 0·001 at 25°. Soluble in amyl alcohol 0·008 at 25°.

Beryllium palmitate.—Be(OH)$\overline{\text{Pa}}$. Soluble in alcohol 0·004 at 25°. Soluble in methyl alcohol 0·042 at 25°.

Calcium palmitate.—Soluble in water 0·003, in alcohol 0·01.

Cerous palmitate.—Insoluble in water. Soluble 0·8 in ether. Slightly soluble in cold turpentine (0·18) (Morrell, *J.C.S.*, 1918, 113, 116).

Lead palmitate.—M.Pt. 112·2°–112·4°. Soluble in water 0·005 at 35°. Soluble in alcohol 0·001 at 35°, 0·012 at 50°. Soluble in methyl alcohol 0·05 at 15·5°, 0·076 at 35°, 0·093 at 50°. Soluble in ether 0·01 at 14·5° and 35·5°, 0·033 at 50°. Soluble in benzene 0·009 at 15°.

Lithium palmitate.—M.Pt. 224°–225°. Soluble in water 0·01 at 18°, 0·015 at 35°. Soluble in alcohol 0·096 at 20°, 0·118 at 25·4°, 0·142 at 35°, 0·248 at 50°, 0·391 at 65°. Soluble in methyl alcohol 0·616 at 15·2°, 0·771 at 25°, 1·086 at 34·6,° 1·652 at 50°. Soluble in ether 0·007 at 15·5° and 25°. Soluble in amyl alcohol 0·019 at 16°, 0·033 at 35°, 0·069 at 49·2°. Soluble in chloroform 0·004 at 15°. Soluble in amyl acetate 0·038 at 14·5° and 50°. Soluble in methyl acetate 0·015 at 24·5°. Soluble in acetone 0·434 at 15°, 0·508 at 25°, 0·537 at 35°.

Magnesium palmitate.—M.Pt. 121°–122°. Soluble in water 0·005 at 15°, 0·009 at 50°. Soluble in alcohol 0·034 at 15°, 0·058 at 25°, 0·085 at 35°, 0·151 at 50°. Soluble in methyl alcohol 0·227 at 15°, 0·336 at 25°, 0·500 at 51·5°. Soluble in ether 0·004 at 25°. Soluble in ethyl acetate 0·004 at 15°, 0·013 at 50°. Soluble in acetone 0·166 at 15°, 0·160 at 25°. Soluble in amyl alcohol 0·043 at 15°, 0·066 at 25°, 0·104 at 35°, 0·263 at 50°. Soluble in amyl acetate 0·039 at 15°, 0·045 at 25°, 0·057 at 34·6°, 0·216 at 50°.

Silver palmitate.—M.Pt. 209°. Soluble in water 0·004 at 35°. Soluble in alcohol 0·007 at 25° and 50°. Soluble in methyl alcohol 0·06 at 15° and 50°. Soluble in ether 0·009 at 15°.

Thallium palmitate.—M.Pt. 115°–117°. (Holde and Selim, *J.S.C.I.*, 1925, 44, B410.)

Methyl palmitate.—M.Pt. 28° (29° *–30). B.Pt. 196° at 15 mm. Soluble in methyl alcohol 29·3 at 15°.

Ethyl palmitate.—M.Pt. 24°. B.Pt. 184·5°–185·5° at 10 mm.

Palmitic anhydride.—M.Pt. 63°–64°. d^{70}, 0·847. n_D^{68}, 1·4364. (*J.S.C.I.*, 1925, 44, B680.)

Stearic Acid. $CH_3(CH_2)_{16}\cdot COOH$

Stearic acid is the commonest constituent of the hard fats. M.Pt. 69·3° (other workers have found figures rising to 71·5.) B.Pt. 291° at 100 mm., 232° at 15 mm. S.G. 1·000 at 11°. n_D^{60}, 1·4322; n_D^{70}, 1·4311. It is insoluble in either cold or boiling water. The solubility in alcohol of various strengths has been studied by various workers, the results obtained by Falciola (*Analyst*, 1911, 36, 23) are given in the following table:

Solubility in Grams per 100 c.c. Stearic Acid

Abs. Alc. °C.					75 per cent. Alc. °C.				50 per cent. Alc. °C.			
50.	40.	30.	20.	10.	40.	30.	20.	10.	40.	30.	20.	10.
..	13·8	4·5	2·0	0·9	0·77	0·39	..	0·15	0·12	0·10	0·08 (23°)	..

For the synthesis of keto-stearic acid see *Report of the Food Investigation Board for* 1923, page 8.

* *J.C.S.*, 1921, 120, 1, 699.

Ammonium stearate. — Falciola (*Analyst*, 1911, 36, 23) found the solubility in alcohol to be as follows:

Temp. °C.	Solubility in grams per 100 c.c. in		
	Abs. Alc.	75 % Alc.	50 % Alc.
50	5·5	..	..
40	1·8	5·0	3·2
30	0·9	1·8	1·2
20	0·5	..	0·5
10	0·3	0·6	0·3

It is soluble in ether 0·1 and in acetone 0·08 both at 15°.

Barium stearate.—Soluble in water 0·004 at 15°, 0·006 at 50°. Soluble in alcohol 0·006 at 16·5°, 0·003 at 50°. Soluble in methyl alcohol 0·042 at 15°, 0·049 at 25°, 0·066 at 35°, 0·077 at 50·5°. Soluble in ether 0·001. Soluble in amyl alcohol 0·007 at 25°.

Beryllium stearate.—Soluble in methyl alcohol 0·04 at 25°.

Calcium stearate.—Soluble in water 0·004 at 15°. Practically insoluble in alcohol.

Cerium stearate.—Insoluble in water. Soluble in ether 0·6. Practically insoluble in cold turpentine (Morrell, *J.C.S.*, 1918, 113, 116).

Lead stearate.—M.Pt. 115·6°–115·8°. Soluble in water 0·005 at 35° and 50°. Soluble in alcohol 0·000 at 25°, 0·004 at 50°. Soluble in methyl alcohol 0·039 at 15·5°, 0·062 at 35°, 0·083 at 50°. Soluble in ether 0·007 at 14·5°. Soluble in ethyl acetate 0·007 at 14°, 0·020 at 50°. Soluble in benzene 0·008 at 15°. Practically insoluble in petroleum ether (40°–60°) at 20° but soluble 0·017 grams in 100 c.c. at the B.Pt. (Neave, *Analyst*, 1912, 37, 399).

Lithium stearate.—M.Pt. 220·5°–221·5°. Soluble in water 0·010 at 16·3° and 35°. Soluble in alcohol 0·072 at 20°, 0·089 at 25·4°, 0·106 at 35°, 0·200 at 50°, 0·333 at 65°. Soluble in methyl alcohol 0·349 at 15·2°, 0·439 at 25°, 0·658 at 34·6°, 1·057 at 50°. Soluble in ether 0·011 at 15·8° and 25°. Soluble in amyl alcohol 0·011 at 16°, 0·028 at 25·7°, 0·031 at 35°, 0·060 at 49·2°. Soluble in chloroform 0·004 at 15·2°. Soluble in amyl acetate ·034 at 14·5°, 0·044 at 50°. Soluble in methyl acetate 0·012 at 24·5°. Soluble in acetone 0·571 at 15°, 0·706 at 25°, 0·663 at 35°.

Magnesium stearate.—M.Pt. 132°. Soluble in water 0·003 at 15°, 0·008 at 50°. Soluble in alcohol 0·017 at 15°, 0·031 at 35°. Soluble in methyl alcohol at 0·084 15°, 0·100 at 25°, 0·166 at 51·5°. Soluble in ether 0·003. Soluble in ethyl acetate 0·004 at 15°, 0·011 at 50°. Soluble in acetone 0·191 at 25°. Soluble in amyl alcohol 0·014 at 15°, 0·018 at 25°, 0·039 at 35°, 0·105 at 50°. Soluble in amyl acetate 0·029 at 15°, 0·046 at 34·6°, 0·115 at 50°.

Potassium stearate.—Soluble in water. Soluble in 94·3 V/V alcohol at 25°, 0·633 gram per 100 grams. Soluble in boiling absolute alcohol, 6·6 grams in 100 grams.

Silver stearate.—M.Pt. 205°. Soluble in water 0·004 at 35° and 50°. Soluble in alcohol 0·007 at 25° and 50°. Soluble in methyl alcohol 0·051 at 15°, 0·055 at 35°, 0·060 at 50°. Soluble in ether 0·007 at 15°.

Thallium stearate.—M.Pt. 119°. (Holde and Selim, *J.S.C.I.*, 1925, 44, B410.)

Methyl stearate.—M.Pt. 38°. (38·5°–39·5°. Levene and Taylor.) B.Pt. 214°–215° at 15 mm. Soluble in methyl alcohol, 4·8 grams in 100 grams at 18°.

Ethyl stearate.—M.Pt. 36·7°. (32·5°–33·5° Levene and Taylor.)

Amyl stearate.—M.Pt. 21°.

Stearic anhydride.—M.Pt. 71°–71·5°; d_4^{82}, 0·8368; d_4^{117}, 0·8149; n_D^{73}, 1·4368 (*J.S.C.I.*, 1925, 44, B.680).

Daturic Acid. $CH_3 \cdot (CH_2)_{15} \cdot COOH$

A so-called " margaric " acid having seventeen carbon atoms was at one time thought to be present in some natural oils, but it was later recognised that this acid was a mixture of various acids, each having an even number of carbon atoms. Of later years, however, a pure acid, having seventeen carbon atoms, seems to have been isolated by Meyer and Beer from datura oil, and hence called daturic acid. M.Pt. 59·5°. The methyl ester has M.Pt. 30°. The ethyl ester has M.Pt. 26·7°–27·5°, B.Pt. 227° at 100 mm., n_D^{60}, 1·4342. This acid has all the properties of the synthetic acid having seventeen carbon atoms. It is more soluble in alcohol than palmitic acid, 100 grams of absolute alcohol dissolving 6·7 grams at 18 and 32·14 grams at 28°. (Ruttan, Eighth International Congress of Applied Chemistry.) This is the only acid with an uneven number of carbon atoms that has been definitely proved to exist in an oil. It is one which is, therefore, of great theoretical interest, and which may very well repay further study.

Arachidic Acid. $C_{21}H_{43} \cdot COOH$ (?)

Arachidic acid is a characteristic constituent of arachis oil, in which it occurs together with lignoceric acid, it is also stated to occur in small quantities in other oils such as rape oil, cacao butter, etc. Until recent years the acid has always been considered to contain twenty carbon atoms arranged in a straight chain, but in 1923, Ehrenstein and Stuewer (*J.S.C.I.*, 1923, 42, 1031A), showed that the isobehenic acid formed by the degradation of lignoceric acid is identical with the arachidic acid isolated from arachis nuts, and that the acid is not $CH_3(CH_2)_{18} \cdot COOH$ as had been previously assumed, but an isodocosanic acid $C_{21}H_{43} \cdot COOH$ or isobehenic acid.

The properties of the natural acid will be given first. M.Pt. 76°–77°. It is only slightly soluble in cold alcohol, but fairly readily soluble in boiling alcohol, from which it can be crystallised: figures for the solubility of the acids isolated from arachis oil are given on page 261. Methyl ester: M.Pt. 54·5°. Ethyl ester: M.Pt., 50°. B.Pt. 284°–286° at 100 mm.

In order that these properties may be compared with the normal acids the following table of melting-points has been compiled showing those of the normal straight chain acids as determined by Levene and Taylor (*J.C.S.*,

Compound.	Carbon Atoms. C_{20}.	C_{22}.	C_{24}.
Ethyl ester . . .	42	49·0	56
Methyl ester . .	46·5*	53·5	59·5†
Acid.	76·5	81·5	85·5†

* This figure is also given by Ehrenstein and Stuewer.

† These figures are also given by Meyer, Brod and Soyka, *J.C.S.*, 1913, 104, i, 1151.

1924, 126, i, 827) on synthetic acids prepared by them. Average figures have been used.

Morgan and Bowen (*J.S.C.I.*, 1924, 43, 346T) give for *n*-eicosanic acid ($C_{20}H_{40}O_2$) M.Pt. 75°, M.Pt. of methyl ester 45·5°–46·5°, M.Pt. of ethyl ester, 41·5°, which figures are practically confirmed by Adam and Dyer (*J.C.S.*, 1925, 127, 70) with 75° for the acid, 41·5°–42·5° for the ethyl ester and 46°–47° for the methyl ester.

These figures would seem to prove fairly conclusively that arachidic acid is not a normal C_{20} acid, and although its exact constitution has not yet been elucidated it would seem to be an isobehenic acid containing the same group as lignoceric.

Behenic Acid. $CH_3(CH_2)_{20}\cdot COOH$

Behenic acid occurs in ben oil and possibly, in small quantities, in other oils. It was first studied by Voelcher in 1848. The M.Pts. of mixtures of behenic acid with stearic, palmitic and oleic acids have been determined by Twitchell (*Analyst*, 1914, 39, 448), and are given under palmitic acid on page 25. The natural acid has been studied by Toyama (*J.C.S.*, 1922, 122, i, 1111), and the synthetic acid by Levene and Taylor (*Ibid.*, 1924, 126, i, 827), whose results are in excellent agreement. The acid has M.Pt. 81°–82°, and dissolves in alcohol 0·1, and in ether 0·2 at about 15°. The methyl ester melts at 54° and the ethyl ester at 50° (48·5°–49·5°, Levene and Taylor; 50°–50·5°, Toyama; 48°–49°, Voelcher). The amide melts at 111°–112°, the anilide at 101°–102° (Toyama).

Lignoceric Acid. $C_{24}\cdot H_{48}O_2$

Lignoceric acid occurs in arachis oil along with arachidic acid. It is also present in rotten oak bark (Sullivan, *J.C.S.*, 1917, 112, i, 8), Sphingomyelin (Levene, *ibid.*, 1913, 104, i, 917), and in Galician lard paraffin (Bergmann, *ibid.*, 1918, 114, i, 285). This acid has not a straight chain, and is an isotetracosanic acid this having been shown by Levene and West (*ibid.*, 1914, 106, i, 1123; *J.S.C.I.*, 1924, 43, B838), who obtained by reduction of lignoceric acid a tetracosane which had M.Pt. 51°–51·5°, whereas *n*-tetracosane has M.Pt. 55°. The melting-point of the synthetic acid and also the melting-point of the synthetic straight chain acid differ considerably from the natural acid (cf. page 30).

Brigl and Fuchs (*J.C.S.*, 1922, 122, i, 712) state that they have obtained lignoceric acid from beechwood tar, and this is supported by Hall and Hermann. The acid isolated by the former workers had M.Pt. 78°–91°. They state that this is a mixture of two acids, one of which has M.Pt. 85°, and is identical with *n*-tetracosoic acid (methyl ester M.Pt. 60°). They suggest that the other constituent is also a *n*-tetracosoic acid of M.Pt. 74°, the isomerism being due to the possibility of the carbon chain existing as a right-handed and also as a left-handed spiral, but there does not seem to be much evidence to support this idea.

Levene, Taylor and Haller (*Analyst*, 1924, 49, 542) have confirmed their opinions. They have been unable to obtain a M.Pt. of more than 81° for the natural acids after the most extensive method of purification, whilst the straight chain synthetic acid ($C_{24}H_{48}O_2$) has M.Pt. 85·5°. They give their opinion that beechwood tar is possibly not a suitable material for the preparation of the acid, their samples having been obtained from arachis oil, and also from cerebrosides.

Heiduschka and Pyriki (*J.S.C.I.*, 1925, 44, B137), found that a sample

of lignoceric acid obtained from arachis oil had M.Pt. 77·5° although they agree with the formula $C_{24}H_{48}O_2$. This M.Pt. is probably too low, although there is always the possibility that the constitution of the acid may vary in oils from different sources.

The natural acid has, according to other workers, M.Pt. 80°–82°. Methyl ester M.Pt. 56·5°–57°. Ethyl ester M.Pt. 55°–56°, B.Pt., 305° at 15 mm.

Acids of the General Formula. $C_nH_{2n-2}O_2$

The most important members of this series are oleic acid and its isomers, but several others occur in smaller quantities in nature. Thus myristoleic acid

$$CH_3\cdot(CH_2)_7\cdot CH=CH\cdot(CH_2)_3\cdot COOH$$

has been isolated from sperm oil (Tsujimoto, *J.S.C.I.*, 1923, **42**, 276A), having B.Pt. 190°–200° at 15 mm., S.G. 0·908 at 15°, n^{15} 1·4566 and iodine value 106·8, whilst Tiglic acid

$$CH_3\cdot CH=C(CH_3)\cdot COOH$$

which has M.Pt. 64·5° and B.Pt. 198·5° is present to a considerable extent in croton oil.

Hypogæic acid, $C_{16}H_{30}O_2$, is said to be present in some oils although there is some doubt. M.Pt. 33°–34°. B.Pt., 236° at 15 mm. An isomeride, palmitoleic acid, occurs to a considerable extent in whale oil. It gives a solid isopalmitoleic acid having M.Pt. 21°–22° under the same experimental conditions as oleic acid forms elaidic acid.

Oleic Acid

$$\begin{matrix} CH_3\cdot(CH_2)_7\cdot CH \\ \| \\ COOH\cdot(CH_2)_7\cdot CH. \end{matrix}$$

Oleic acid is the most common unsaturated acid present in oils—it constitutes the greater part of the acids of the liquid non-drying oils. A large number of isomerides are, of course, possible, some of which are known, but the one which is of greatest importance is elaidic acid, which is the geometrical solid isomeride of ordinary liquid 9 : 10 oleic acid from which it may be produced by the action of nitrous acid fumes. The reverse change can be brought about by heating elaidic acid under pressure with sulphurous acid.

It has been customary to describe oleic acid as the trans acid for reasons which are more or less obscure, but Armstrong and Allan have suggested that this nomenclature be reversed in accord with the more usual custom of regarding the more stable higher melting form as the *trans* isomeride, which would, therefore, mean that this structure would be assigned to elaidic acid. Müller and Shearer as the result of X-ray measurements regard elaidic acid as a *trans* compound.

$$\begin{matrix} CH_3\cdot(CH_2)_7\cdot CH \\ \| \\ HC(CH_2)_7\cdot COOH. \end{matrix}$$

Elaidic—*trans* acid.

$$\begin{matrix} CH_3(CH_2)_7\cdot CH \\ \| \\ COOH\cdot(CH_2)_7\cdot CH \end{matrix}$$

Oleic—*cis* acid.

Perfectly pure oleic acid is most difficult to prepare and is probably still unknown. Lapworth and Pearson (*Reports of the Food Investigation*

Board, London, H.M. Stationery Office, 1921, page 29; 1922, page 44) have studied this matter at considerable length, but they have not yet prepared an oleic acid which could be looked upon as pure, palmitic acid being retained with great persistence. This work is being continued (cf. *J.S.C.I.*, 1925, 44, B249). As in all probability all the samples of oleic acid hitherto examined have been more or less impure no useful purpose will be served by giving all the properties of the acid and its salts so far published; those that are given below must be accepted with a certain amount of reserve. Lapworth and Pearson have found, by a method of extrapolation, that the ordinary setting-point of oleic acid is 13° or very slightly above. Oleic acid is, however, dimorphous the second form melting two or three degrees higher. These workers state that " it is clear that oleic acid forms at least two, and probably three, series of solid solutions with palmitic acid. Owing to the sluggishness with which one series is transformed into another, highly deceptive results are obtained when attempts are made to determine the relations between the setting-point curves of two series, and setting-points have consequently been abandoned as tests of composition of mixtures."

The following abstract (*Analyst*, 1925, 50, 470) has been made of a paper by Lapworth and Mottram (*J.C.S.*, 1925, 127, 1628) on the determination of oleic acid :

> " Even comparatively impure samples of oleic acid may be analysed as follows, particularly with regard to the determination of all saturated fatty acids not volatile in steam. A clear solution of the sodium salts from about 5 grms. of the ' oleic acid ' is cooled, diluted with 4 litres of ice-cold water, and 400 c.c. of 1 per cent. potassium permanganate solution slowly added at 10° C., with continual shaking. After 5 minutes sulphur dioxide is used to decolorise the liquid, and 150 c.c. of concentrated hydrochloric acid are added. The crude solid dihydroxystearic acid thus precipitated is drained, washed with about 50 c.c. of petroleum spirit (the washings being kept), and dried to constant weight, then extracted with 100–500 c.c. of petroleum spirit (B.Pt. 70–80° C.), the whole cooled, and filtered, the residue of nearly pure dihydroxystearic acid washed, and the washings and extract combined and evaporated. The residue from these is distilled in steam to remove any volatile fatty acids, and the non-volatile acids are then extracted with petroleum spirit. The solvent is evaporated, and the acids heated on a water bath to constant weight."

The acid is insoluble in water, but readily soluble in alcohol. It is readily attacked by ozonised air forming ozonides and perozonides. Each molecule of oleic acid is capable of combining with two atoms of halogen. When fused with caustic alkalies palmitic acid and acetic acid are formed the breaking down not taking place at the double bond as was at one time thought. d^{15} 0·898; B.Pt., 232·5° at 15 mm.; n_D^{70}, 1·4415; n_D^{20}, 1·4620.

The melting-points of mixtures of oleic with saturated fatty acids have been studied by the following : Carlinfanti and Levi-Malvano (*Analyst*, 1910, 35, 30), Twitchell (*ibid.*, 1914, 39, 448), Meldrum (*ibid.*, 1913, 38, 579), these are given under palmitic acid (page 26), whilst Pascal (*J.S.C.I.*, 1914, 33, 602) has determined the refractive indices of mixtures of palmitic, stearic and oleic acids. The following are certain other papers that have appeared dealing with the properties of oleic acid :

> " On the Ozonides of Oleic Acid." Harries and Thieme. *Analyst*, 1906, 31, 412.

" A Spectrum Reaction for Oleic Acid." Lifschutz. *Analyst*, 1908, 33, 479.
" Separation of Oleic from Stearic and Palmitic Acids." Falciola. *Analyst*, 1911, 36, 23.
" The Alleged Dimorphism of Oleic Acid." Kirschner. *J.S.C.I.*, 1912, 31, 593.
" The Relation between Iodine Value and Structure of Members of the Oleic Acid Series." Ponzio and Gastaldi. *J.S.C.I.*, 1912, 31, 884.
" New Isomerides of Oleic Acid." Fokin. *J.S.C.I.*, 1913, 32, 96.
" The Oxidation of Oleic Acid in Sunlight." Canzoneri and Bianchini. *Analyst*, 1914, 39, 255.
" The Action of Halogens on Oleic Acid." Mergen and Winogradoff. *Analyst*, 1914, 39, 311.
" Isomeric Oleic Acids." Eckert and Halla. *J.S.C.I.*, 1914, 33, 32.
" Catalytic Reduction of Oleic Acid by Hydrogen and Nickel." Shaw. *J.S.C.I.*, 1914, 33, 771.
" The Esters of Oleic Acid and their Hydrogenated Products." Ellis. *J.S.C.I.*, 1917, 36, 39.
" The Products of Hydrogenation of Oleic Acid." Moore. *J.S.C.I.*, 1919, 38, 320T.
" Properties of the Oleates of some of the Heavy Metals." Albuquerque. *J.C.S.*, 1920, 118, i, 216.
" A Degradation Product of Oleic Acid." Lifschutz. *J.S.C.I.*, 1921, 40, 478A.
" Relation of Oleic Acid to Elaidic Acid." Nicolet. *J.S.C.I.*, 1922, 41, 109A.
" The Catalytic Decomposition of Oleic Acid." Mailhe. *J.S.C.I.*, 1922, 41, 334A.
" The Action of the Brush Discharge on Oleic Acid." Eichwald. *J.S.C.I.*, 1922, 41, 824A.
" The Separation of Methyl Oleate from Methyl Linolate." *J.S.C.I.*, 1923, 42, 364A.
" Oleic Alcohol and its Composition." Toyama. *J.S.C.I.*, 1924, 43, B223.

Ammonium oleate.—Soluble in absolute alcohol 100 at 50°, 59 at 10°; in 75 per cent. alcohol 8·2 at 10°, 10·9 at 30°. Soluble in ether 16·9 at 15°. Soluble in acetone 4·7 at 15° (Falciola, *Analyst*, 1911, 36, 23).

Barium oleate.—Insoluble in water and almost so in alcohol. Soluble in boiling benzene containing traces of water from which solution the salt crystallises almost entirely on cooling.

Calcium oleate.—Soluble in water 0·009 at 15°. Zink and Liere, Fahrion (*J.S.C.I.*, 1915, 34, 622; 1916, 35, 932). Insoluble in ether.

Cerous oleate.—Completely soluble in ether (Morrell, *J.C.S.*, 1918, 113, 117).

Lead oleate.—White powder. M.Pt. 45°–50°—which is considerably lower than the figure quoted by Gottlieb (80°). It is very soluble in ether and petroleum ether, which property is made use of in the separation of saturated and unsaturated acids.

Lithium oleate.—Soluble in hot alcohol. Insoluble in ether, carbon bisulphide and benzene. Soluble in water 0·067 at 18° and 0·13 at 25°. Soluble in 99·5 per cent. alcohol, 0·91 at 18° and 1·01 at 25°.

Magnesium oleate.—Soluble in water 0·022 at 15° (Fahrion, *J.S.C.I.*,

1916, 35, 932). Soluble in 90 V/V alcohol 8·60 grams per 100 grams at 25° (Thomas and Yu, *J.S.C.I.*, 1923, 42, 233A).

Potassium oleate.—Soluble in water about 25 at 15°. Soluble in 94·3 V/V alcohol at 25° 41·1 grams per 100 grams. Soluble in boiling ether about 3.

Sodium oleate.—M.Pt. 232°–235°. Soluble in water 10, in 92 per cent. alcohol 5, in boiling ether 1 (cf. Pictet and Potok, *J.S.C.I.*, 1919, 38, 939A).

Thallium oleate.—M.Pt. 83°. Holde and Selim (*J.S.C.I.*, 1925, 44, B410).

Oleic anhydride.—In silver scales. M.Pt. 22·2°. Holde and Tacke. *J.S.C.I.*, 1921, 40, 817A).

Oleic anilides.—Constants and properties of various (de Conno, *Analyst*, 1917, 42, 213).

Methyl oleate.—d^{18}, 0·879. B.Pt. 212°–213° at 15 mm.

Ethyl oleate.—d^{15}, 0·871.

Elaidic Acid

$$CH_3\cdot(CH_2)_7\cdot CH$$
$$\|$$
$$HC(CH_2)_7\cdot COOH$$

This acid, which is produced by the action of nitrous acid on ordinary oleic acid, is, as has already been said, a geometrical isomer of the latter. The acid may be crystallised from alcohol, giving plates which melt at 44·5° (Geitel, *Analyst*, 1899, 24, 258). d^{80}_{40}, 0·850. B.Pt. 234° at 15 mm.

The metallic salts of elaidic acid have not been extensively studied. The barium, lead and silver salts are insoluble in water and only slightly soluble in alcohol, ether or benzene. Solubility of the lead salt in absolute alcohol 0·01 at 15°. Methyl elaidate has d^{18}, 0·872, whilst ethyl elaidate, has d^{18}, 0·868. Cerous elaidate is soluble in ether 1·07 (Morrell, *J.C.S.*, 1918, 113, 117).

Iso-oleic Acids. $C_{18}H_{34}O_2$

Several other isomeric oleic acids have been isolated from various natural products or prepared by chemical action. Thus on distilling hydroxystearic acid or by hydrogenation of oleic acid a mixture of acids is produced which probably contains the 11·10 oleic acid; parsley-seed oil contains an acid, petroselinic acid, which is probably 6·7 oleic acid, whilst other acids are said to have been isolated from liver lecithin, from rape oil and from cheiranthus oil. The whole question is quite unsatisfactory and needs further investigation as has been shown by numerous later investigations. Thus Grabner (*J.S.C.I.*, 1921, 40, 896A) has stated that the so-called rapic acid of rape oil is identical with oleic acid and has no separate existence. Gadoleic acid has been found by Bull to occur in notable quantities in cod-liver oil, herring oil and other fish oils. It had M.Pt. 24·5°. The presence of this acid in herring oil has been confirmed by Lexow (*J.S.C.I.*, 1921, 40, 438A). Cf. composition of hydrogenated oils, page 470.

Erucic Acid. $C_{22}H_{42}O_2$

$$CH_3\cdot(CH_2)_7\cdot CH$$
$$\|$$
$$COOH\cdot(CH_2)_{11}\cdot CH$$

Erucic acid is the characteristic acid of rape oil. It may be crystallised from alcohol. M.Pt. 33°–34°. B.Pt. 264° at 15 mm. The lead salt is only slightly soluble in ether, resembling in this property the saturated acids

rather than the unsaturated. Methyl erucate has d^{15}, 0·874, n^{20}, 1·4558, B.Pt., 221°–222° ar 5 mm. The acid in nearly all its properties strongly resembles oleic acid. Thus, on treatment with the fumes of nitrous acid it is transformed into brassidic acid, its geometrical isomer. Cf. Holde and Wilke (and Schmidt), *J.S.C.I.*, 1922, 41, 260A, 424A, 598A, 825A; 1923, 42, 1139A. For structure, cf. Mascarelli (and Sanna), *ibid.*, 1916, 35, 262; 1917, 36, 603, and derivatives, *ibid.*, 1922, 41, 988A and *J.C.S.*, 1922, 122, i, 1111, and *Analyst*, 1917, 42, 213. For ammonium erucate, see *Analyst*, 1911, 36, 114, *J.C.S*, 1916, 110, i, 707. For ethyl erucate, see *J.C.S.*, 1922, 122, i, 1111; *J.C.S.I.*, 1923, 42, 896A.

Brassidic Acid. $C_{22}H_{42}O_2$

$$CH_3\cdot(CH_2)_7\cdot CH$$
$$HC\cdot(CH_2)_{11}\cdot COOH$$

Formed, as stated above, by treating erucic acid with nitrous acid. M.Pt. 65°. B.Pt. 265° at 15 mm. The ethyl ester has M.Pt. 30°–30·5°, n_D^{35}, 1·4587. (*J.S.C.I.*, 1922, 41, 825A; 1923, 42, 896A). The anhydride has M.Pt. 64°; d_4^{70}, 0·835. For structure see references under erucic acid above.

Unsaturated Acids. $C_nH_{2n-2}O_2$

It is generally considered that our knowledge of the saturated fatty acids is fairly complete, although recent results would point to the fact that there is still a considerable amount of work to be done in this field. Our knowledge of the acids of the $C_nH_{2n-2}O_2$ series is far less complete, as will be gathered from the outline presented above, but it can safely be said that very little is known of the acids which are more unsaturated than oleic acid. This is largely due to the extreme difficulty of the determination of constitutional formulæ in cases where the substance may not be stable, where double bonds may readily wander, and where the total number of possible isomers, both constitutional and geometrical, is enormous. A certain number of the more highly unsaturated acids have been examined and their properties determined, but in most cases the constitutional formulæ are either uncertain or unknown.

Acids of the General Formula. $C_nH_{2n-4}O_2$

Linolic Acid. $C_{18}H_{32}O_2$

This acid, also known as linoleic, occurs widely in the drying and semi-drying oils from which it may be prepared by bromination of the mixed fatty acids recrystallising the product from petroleum ether, and reducing this tetrabromide so prepared in methyl alcohol solution to methyl linolate. The acid has sol.pt. below −18°, B.Pt., 229° at 15 mm. The acid is readily soluble in alcohol and ether. The solid tetrabromide has M.Pt. 114°, but a liquid tetrabromide readily soluble in petroleum ether (in contradistinction to the solid which crystallises well from this solvent) is also formed. The acid and its anhydride have been studied by Holde and Weill (*J.S.C.I.*, 1923, 42, 938A) who found iodine value (Hanus), 178·6; acid value, 196·7; sp. gr. at 20° C./4° C., 0·9025; n_D^{20} = 1·4711; M.Pt. −25° to −24° C. Later, Holde and Gentner (*J.S.C.I.*, 1925, 44, B600, B680), found M.Pt., −8° to −7°; B.Pt., 202° at 1·4 mm.; Sp. gr. 0·9038 at 18°/4°, 0·9007 at 22·8°/4°; $n_D^{11·5}$ 1·4715, $n_D^{21·5}$ 1·4683. The anhydride was found to have M.Pt. −3·5° to −2·8°; Sp. gr. 0·901 at 23·8°/4°; $n_D^{11·5}$ 1·4775.

André (*J.S.C.I.*, 1923, 42, 364A) has indicated a method of separating methyl linolate from methyl oleate by fractional distillation.

Cf. also " The Metal content of Various Commercial Linoleates (Linolates)." Radcliffe and Palmer, *J.S.C.I.*, 1915, 34, 644. The occurrence and synthesis of mixed glycerides of linolic acid. Grün and Schönfeld, *ibid.*, 1916, 35, 366. Takahashi, *J.C.S.*, 1919, 116, i, 468; 1921, 120, i, 303. Coffey, *ibid.*, 1921, 119, ii, 1306, 1408; Salway, *ibid.*, 1916, 109, i, 138.

Ammonium linolate.—Begins to melt at 57°–58°. Readily soluble in methyl alcohol. Soluble in ammoniacal absolute alcohol at 0° about 35. Soluble in hot benzene and acetone and in cold chloroform and carbon tetrachloride. Sparingly soluble in ether. Falciola, *Analyst*, 1911, 36, 114.

Various metallic salts have been examined, but not extensively. Many of them are soluble in alcohol, ether and benzene. Barium linolate is readily soluble in benzene, which sharply distinguishes it from barium oleate. Lead linolate is readily soluble in ether. Cerous linolate is completely soluble in ether (Morrell, *J.C.S.*, 1918, 113, 117).

The methyl ester boils at 210°–211° at 15 mm.; $d_{\frac{4}{4}}^{18}$, 0·889.

Elæostearic Acid. $C_{18}H_{32}O_2$

Elæostearic acid occurs in tung oil. It apparently exists in two forms known respectively as α and β—elæostearic acid—the tetrabromides of the two forms are identical (Morrell, *J.S.C.I.*, 1912, 31, 1189) (Nicolet, *J.C.S.*, 1921, 120, i, 660). Majima reduced the acid to stearic acid and thus proved that it (probably) contains a normal chain (*J.S.C.I.*, 1912, 31, 998). There is some doubt as to whether the acid is $C_{18}H_{32}O_2$ or $C_{18}H_{30}O_2$, the matter having not yet been settled (cf. Maquenne, *Analyst*, 1924, 49, 105). The α acid has M.Pt. 48° and the β acid 71°–72°, the latter having an experimental iodine value of 172. The cerium and lead salts have been studied by Morrell (*J.C.S.*, 1918, 113, 116; 1922, 122, i, 982. *J.S.C.I.*, 1922, 41, 328T; 1915, 34, 105; 1918, 37, 181T). The formula of the acid is discussed by Böescken and Ravenswaay, *J.S.C.I.*, 1925, 44, B813.

Tariric Acid. $C_{18}H_{32}O_2$

The acid has the same empirical formula as linolic acid, but is quite different in constitution as it has one triple bond; it is not very widely distributed in nature. The constitution has been studied by Arnaud and his co-workers who give it the formula

$$CH_3\cdot(CH_2)_{10}C\equiv C(CH_2)_4\cdot COOH$$

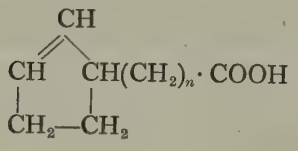
It melts at 50·5°. It absorbs four atoms of bromine, the tetrabromide melting at 125°.

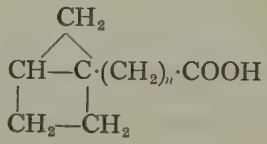
Hydnocarpic Acid. $C_{16}H_{28}O_2$

This acid has again the same empirical formula as the corresponding member of the oleic series, but its structure is totally different as, in this case, a 5 atom ring is present, and also because of the presence of an asymmetric carbon atom, which causes the acid to be optically active. The acid occurs together with chaulmoogric (see below) in hydnocarpus and chaulmoogra oils.

The constants of the acid have been studied by Brill and Williams (*J.S.C.I.*, 1918, 37, 166A) and by Dean and Wrenshall (*Analyst*, 1921, 46, 52) who found: M.Pt. 59°; iodine value, 99·9–100·2; sap. val. 218·2–222·7; $[\alpha]_D^{30}$ in chloroform +67·6° to +67·7° (B. & W.)+68·1° (D. & W. no temp. given). (Cf. Rakuzin and Flier, *J.C.S.*, 1916, 110, i, 273.)

The constitution of this acid and of chaulmoogric acid has been studied by Power and Barrowcliff (*J.C.S.*, 1905, 87, 577), who have ascribed the following tautomeric formulæ to both:





Chaulmoogric Acid. $C_{18}H_{32}O_2$

This acid occurs in chaulmoogra, hydnocarpus and lukrabo oils. The constants of the acid have been determined by Brill and Williams (*J.S.C.I.*, 1918, 37, 166A), by Dean and Wrenshall (*Analyst*, 1921, 46, 52), and by Goulding and Akers (*J.S.C.I.*, 1913, 32, 704). M.Pt. 68°. Iodine value 89·5–90·1 (B. and W.), 90·1 (D. and W.), 90·5 (G. and A.). Sap. Val., 200·5–203·4 $[\alpha]_D^{30}$ in chloroform +58·1° to +59·05° (B. and W.), +56° D. and W., no temp. given), $[\alpha]_D^{17}$, +60° (G. and A.).

Methyl chaulmoograte.—M.Pt. 22°. B.Pt. 227° at 20 mm. $d_{\frac{25}{25}}^{25}$° 0·912. $[\alpha]_D$ 55·8°. (Goulding and Akers, *J.S.C.I.*, 1913, 32, 704.)

Ethyl chaulmoograte.—B.Pt. 230° at 20 mm. $d_{\frac{15}{15}}^{15}$° 0·908.

Acids of the General Formula $C_nH_{2n-6}O_2$

Linolenic Acid. $C_{18}H_{30}O_2$

This acid occurs in considerable quantities in the drying oils, particularly in linseed oil. B.Pt. 230°–232° at 17 mm. $d_{\frac{15}{4}}^{15}$. 0·914. There is some evidence of the existence of two isomeric linolenic acid which have been called respectively α and β linolenic acids, but the matter is not yet settled. The oxidation of this acid by means of hydrogen peroxide or perbenzoic acid has been studied by Bauer and Kutscher (*J.S.C.I.*, 1925, 44, B459).

Zinc linolenate.—$((C_{18}H_{29}O_2)_2Zn)_2 \cdot ZnO$. M.Pt. 72–73. Soluble in alcohol 0·9 in the cold, 6·2 at a higher temperature. Cf. Coffey, *J.C.S.*, 1921, 119, ii, 1306, 1408; Salway, *ibid.*, 1916, 109, i, 138.

Methyl linolenate.—B.Pt. 207° at 14 mm. $d_{\frac{4}{4}}^{20}$, 0·892.

Ethyl linolenate.—B.Pt. 132°–133° at 0·001 mm. n_D^{20}, 1·4675.

It is quite possible that other isomers and homologues of linolenic acid occur in nature, but no definite information is at present forthcoming. Owing to the large number of possible isomers the matter is very complicated.

Acids of the General Formula $C_nH_{2n-8}O_2$

The isolation of isanic acid, $C_{14}H_{20}O_2$, and of therapic acid $C_{17}H_{26}O_2$ have both been claimed, but the evidence in their favour is at least not conclusive. Acids of the formula $C_{20}H_{32}O_2$ have also been mentioned. The only important member of this series is clupanodonic acid.

Clupanodonic Acid. $C_{22}H_{34}O_2$ (?)

This acid was first isolated by Tsujimoto (*Analyst*, 1906, 31, 336, 344) from Japanese sardine oil. It is widely distributed in fish and marine animal oils. The oil gives an octobromide having the formula $C_{18}H_{28}Br_8O_2$. The mixed fatty acids of fish oils contain up to 14 per cent. The octobromide is almost insoluble in alcohol, ether, and glacial acetic acid. It decomposes at about 200° without melting. It readily becomes oxidised in the air, changing to a dry mass.

There is some doubt as to the constitution of this acid for whilst Schmidt-Nielsen (*J.S.C.I.*, 1922, 41, 300A) gives it the formula $C_{18}H_{28}O_2$, Tsujimoto, although at first agreeing with this, in later work (*ibid.*, 1920, 29, 825A; 1922, 41, 719A; 1923, 42, 1185A) considers that $C_{22}H_{34}O_2$ is the correct formula, which has been confirmed by Eibner and Semmelbauer, *ibid.*, 1924, 43, B986. Cf. Riedel, *J.C.S.*, 1914, 106, i, 1123. $d\frac{15°}{4}$, 0·939; $d\frac{20°}{4}$, 0·936. n_D^{40}, 1·4948. Liquid at −50°; semi-solid at −78°. The methyl ester is a light yellow liquid B.Pt. about 222° at 5 mm. It does not readily distil with steam (Tsujimoto, *J.S.C.I.*, 1913, 32, 96). Occurs in the brain (Grey, *J.C.S.*, 1913, 104, i, 552).

Arachidonic Acid. $C_{20}H_{32}O_2$

An acid of this formula was discovered by Hartley (*J. of Physiol.*, 1909, 38, 353) to which the name arachidonic acid was ascribed by Lewkowitsch. It occurs in animal tissues, a method for its determination in which has been described by L. G. Wesson (*Analyst*, 1925, 50, 578).

Hydroxy Acids

A number of acids occur in nature having one or more hydroxyl groups present in the molecule; both saturated and unsaturated hydroxy acids are known. The saturated acids are not particularly important, although sabinic acid ($C_{12}H_{24}O_3$), juniperic acid ($C_{16}H_{32}O_3$), lanopalmic acid ($C_{16}H_{32}O_3$) and cocceric acid ($C_{31}H_{62}O_3$) have been described.

The Unsaturated Mono-Hydroxy Acids

1. Ricinoleic Acid

The most important of the unsaturated hydroxy acids, in fact, the most important of all the hydroxy acids, is ricinoleic acid, $C_{18}H_{34}O_3$, which occurs in large quantities in castor oil and to the glyceride of which this oil owes its characteristic property. It contains an asymmetric carbon atom and its compounds are therefore optically active. The constitution has been dealt with of recent years by Jones (*J.S.C.I.*, 1917, 36, 359), by Stosius and Wiesler (*J.S.C.I.*, 1921, 40, 18A), and by Nicolet and Pelc (*J.C.S.*, 1922, 122, i, 644). The properties of the pure acid have not been obtained with certainty. The figures usually quoted are S.G. 0·951, M.Pt. 4°–5°. $[\alpha]_D$, 6·7°. The preparation of the pure acid has been undertaken by Holde (*J.S.C.I.*, 1923, 42, 896A).

Esters have been prepared by Haller (*Compt. Rendu.*, 1907, 144, 462), who found the following properties.

TABLE IX.—CONSTANTS OF THE RICINOLEIC ESTERS

Ester.	B.P., 10 mm.	$D^{15°}$.	Specific Rotation.	$n_D^{15°}$.
Methyl	225°–227°	0·927	5° 2′	1·4645
Ethyl	227°–230°	0·918	4° 48′	1·4830
n-Propyl	233°–236°	0·912	4° 35′	1·4624
Isobutyl	239°–241°	0·908	4° 22′	1·4621

When treated with nitrous acid ricinoleic acid is changed into its geometric isomeride, ricinelaidic acid as in the case of oleic acid. M.Pt. 52°–54°. $[\alpha]_D = +6·67°$ in absolute alcohol at a concentration of 12 per cent.

THE DIHYDROXY ACIDS

Dihydroxystearic acid, $C_{18}H_{36}O_4$, occurs in castor oil to the extent of about 1 per cent., M.Pt. 141°–143°. The methyl ester has M.Pt. 106°–108°. Thoms and Deckert have stated that they have isolated a new acid from hydrogenated castor oil.

Lapworth and Mottram (*J.C.S.*, 1925, 127, 1628, 1987) have confirmed the nearly quantitative conversion of oleic acid into dihydroxystearic acid by means of an alkaline solution of 1 per cent. potassium permanganate and have shown that continued oxidation in the cold converts the dihydroxystearic acid into suberic, *n*-octoic and oxalic acids. In hot solutions mainly suberic and azelaic acids are formed. The oxidation of this acid by hydrogen peroxide and perbenzoic acid has been studied by Bauer and Kutscher (*J.S.C.I.*, 1925, 44, B459).

Another acid of the same series, lanoceric acid, $C_{30}H_{60}O_4$, has been obtained from wool wax.

Other acids have been isolated from natural products or prepared synthetically, but as yet they are not of sufficient importance to warrant extended discussion.

3. ALCOHOLS

THE STEROLS

The sterols are complex alcohols with a cyclic constitution which occur in small quantities in most of the vegetable and animal fats. Those occurring in animal fats differ from those occurring in vegetable fats and this fact can be made use of for determining the source of an unknown oil or for the detection of animal oils in vegetable oils and *vice versa*. The following sterols are known:

Name.		Formula.	M.Pt.	Occurrence.
Cholesterols	Cholesterol .	$C_{27}H_{46}O$	148°–150°	Animal oils
	Isocholesterol	$C_{27}H_{46}O$	137°–138°	Wool fat
	Bombicesterol	$C_{26}H_{44}O·H_2O$	148°	Chrysalis oil
Phytosterols	Sitosterol .	$C_{27}H_{46}O$	135°	Maize oil
	Brassicasterol .	$C_{28}H_{46}O·H_2O$	148°	Rape oil
	Stigmasterol .	$C_{30}H_{48}O·H_2O$	170°	Calabar bean
	Coprosterol .	$C_{25}H_{44}O$	98°–100°	Sewage fats

The sterols may be detected by means of the reaction with digitonin, which is described fully under the phytosteryl acetate test on page 124. Two colour reactions have lately been described by Whitby (*Analyst*, 1923, 48, 226) which are stated to be delicate and distinctive. It was at one time thought that the cholesterols were typical of the animal fats and the phytosterols of the vegetable fats, and that the discovery of either one or the other of these bodies in an oil pointed unmistakably to the presence of the corresponding fat. This is undoubtedly very largely the case, but the following remarks of Steuart (*Analyst*, 1923, 48, 155) should be very carefully read in this connection. " An examination of the sterol prepared from a sample of fat will show definitely whether the fat is of purely animal origin or whether the vegetable fat is present. The results of this work indicate that the sterol acetate examination cannot be used to demonstrate the presence of animal fats in mixtures containing vegetable oils. Marcusson and Meyerheim (1916) found from 8 to 14 per cent. of sterol in the unsaponifiable matter of animal fats, *e.g.*, cod-liver oil and tallow, and 33 to 55 per cent. in that of vegetable oils. This suggested that the proportion of sterol in the unsaponifiable matter of a margarine fat might give some indication as to its origin; but such a hope can no longer be entertained."

The properties of the various sterols so far as they are at present known are given below. Lewkowitsch divides the sterols into zoosterols (the animal sterols) and phytosterols (the vegetable sterols). A useful summary of the properties and a system of classification is given by Dorée (*Biochem. J.*, 1913, F, 616). The possible relationship of sterol and vitamine A content has been discussed by Drummond, Rosenheim and Coward (*J.S.C.I.*, 1925, 44, 123T).

Cholesterol.—White crystals crystallising from hot alcohol or chloroform in anhydrous needles. Insoluble in water, sparingly soluble in dilute alcohol, easily soluble in ether, carbon bisulphide and chloroform. Soluble in absolute alcohol. The M.Pt. is given by Bömer as 148·5°–150·8° corr. Polenske, in an extended investigation of 284 cholesterols isolated from 254 different specimens of lard, found the following corrected M.Pts.

No. of Samples.	M.Pt. °C.
2	145
15	146–146·5
36	146·5–147
185	147–148
15	148
1	148·5

Hepburn (*J.S.C.I.*, 1913, 32, 989) gives the M.Pt. of cholesterols from different sources as 147·4°–149·1°. It is strongly lævo-rotatory. $[\alpha]_D$ in chloroform solution −34·3° to −36·6°.

The bromine compounds have been investigated by Windaus (*Analyst*, 1906, 31, 411) who finds that the dibromide is sparingly soluble in a mixture of ether and glacial acetic acid and that this fact may be made use of to separate cholesterol from phytosterol.

Various qualitative colour reactions for the sterols have been proposed from time to time. In the main these reactions are given with varying shades and intensities by all the sterols so that they cannot be used for distinguishing between, say, cholesterol and phytosterol. Schulze suggested colours with strong nitric acid and sulphuric acid respectively, but the colours given are not specific. The Hager-Salkowski reaction consists in dissolving a small

amount of sterol in chloroform, adding an equal amount of conc. sulphuric acid and shaking the mixture when the chloroform layer assumes a red colour turning to purple. The Liebermann-Burchard reaction consists in dissolving a little sterol in about 2 c.c. of chloroform and adding 20 drops of acetic anhydride and 1 drop of conc. sulphuric acid when a reddish violet colouration is produced. Golodetz (*Analyst*, 1908, 33, 133) has proposed a colour test with sulphuric acid and formaldehyde, whilst Whitby (*Analyst*, 1923, 48, 226) makes similar suggestions and also gives a modification of the acetic anhydride reaction.

Lifschutz and Grethe (*J.S.C.I.*, 1914, 33, 929), describe the preparation and properties of oxycholesterol, M.Pt. 107°–113°. They say that it may be distinguished from cholesterol by treating its solution in glacial acetic acid, with a few drops of concentrated sulphuric acid. The red or bluish-violet colour thus produced is changed to bright green on adding ferric chloride solution, and on then adding one or two drops of chromic acid the liquid becomes colourless. Cholesterol does not give this colour reaction.

The digitonin compound has M.Pt. 215°–218°. Oxycholesterol is present in the brain (*Analyst*, 1915, 40, 129) and Rosenheim gives a colour reaction with dimethyl sulphate (*Analyst*, 1916, 41, 284).

Cholesteryl acetate.—The acetic ester is produced by boiling the cholesterol with excess of acetyl chloride. It crystallises in small needles, insoluble in cold alcohol, slightly soluble in boiling alcohol, readily soluble in low boiling petroleum ether. M.Pt. 114°–114·8° (corr.) $[\alpha]_D$ −43°.

Isocholesterol. Occurs together with cholesterol in wool fat. M.Pt. 137°–138°. Insoluble in water and almost so in cold alcohol, in ether, or in petroleum ether. Cohen has claimed to have isolated a sterol from African rubber, which is identical with isocholesterol, and draws the conclusion that no fundamental difference exists between sterols of animal and vegetable origins; this opinion is interesting, taken in conjunction with the views of Steuart (page 41), but has received little, if any, attention. The solutions of this substance are dextro-rotatory $[\alpha]_D$ +60°. Isocholesterol gives the same colour reactions as cholesterol, but the acetate is difficult to obtain in the pure state, although Dorée has found the M.Pt. 134°.

Bombicesterol.—This sterol is stated to occur in chrysalis oil, together with cholesterol. Its M.Pt. is 148 $[\alpha]_D$ −34·9°, which figures are identical with those of cholesterol. The acetate has M.Pt. 129°, and $[\alpha]_D$ −42·7, on which evidence it has been adjudged to have a separate existence.

Sitosterol.—Sitosterol is the typical sterol of plants and is the principal member of that class of phytosterols which has long been considered to be typical of vegetable oils in general. A large amount of confusion has existed in regard to the constitution and properties of the various phytosterols, and even now the exact position of the chemistry of the subject is not particularly clear, and it would appear that the results likely to be obtained from further work on the subject might repay very amply the labour involved.

Sitosterol has M.Pt. 137° $[\alpha]_D$ −23° to −27° according to concentration and solvent. Insoluble in water, slightly soluble in cold alcohol, easily soluble in hot alcohol, ether, chloroform, etc. The colour reactions and bromine compounds are mentioned under cholesterol, on page 41.

Anderson and Nabenhauer (*J.S.C.I.*, 1924, 43, B888) have prepared a highly purified sample of sitosterol (by means of the bromine compound) which had M.Pt. 138°–139°; $[\alpha]_D^{20}$ = −36·69 in chloroform. The acetyl derivative had M.Pt. 130°–131° and $[\alpha]_D^{20}$ = −40·20. Dihydrositosterol has $[\alpha]_D^{20}$ = +25·82.

Sitosterol acetate is given by different observers as having melting-point

varying from 123·5° to 137° which obviously points to the fact that the phytosterol obtained from vegetable oils is not a single substance, but a mixture of substances. Jager and Klamorth give the M.Pt. of pure sitosterol acetate as 127°. Further evidence in favour of this assumption has been obtained by Steuart (*Analyst*, 1923, 48, 155) who finds that the M.Pt. of sterol acetates obtained from vegetable oils varies from 125° to 139°, but that it is possible by recrystallisation to find a fraction of this with M.Pt. as low as 115°. The matter is obviously one which requires considerable further careful investigation (cf. the sterols of maize oil, page 205). Brassicasterol, stigmasterol and coprosterol are said to occur in rape oil, calabar beans and in sewage fats respectively. Very little is known of their composition and properties, and no little confusion exists. Further work on this subject is very desirable. Brassicasterol is said to have M.Pt. 148° and $[\alpha]_D^{18} -64°$, whilst the acetate has M.Pt. 157°−158°. Stigmasterol, M.Pt. 170°, $[\alpha]_D^{25}$ −44·7°; the acetate, M.Pt. 141°. Coprosterol, M.Pt. 95°–100° $[\alpha]_D^{20}$ +24°; the acetate M.Pt. 88° or 114° according to the observer.

CHAPTER V

EXAMINATION AND SEPARATION OF THE FATTY ACIDS

Under certain circumstances and for particular purposes an examination of the fatty acids obtained from a fat by saponification may be useful, and is sometimes necessary. The acids may be prepared in the following manner.

Preparation.—Place 50 grams of the fat (or other suitable quantity) in an extraction flask or porcelain dish and add 20 grams of potassium hydroxide dissolved in about 30 c.c. of water and 50 c.c. of alcohol (Industrial Spirit). Heat the mixture on the water-bath (under a reflux condenser where any oxidation of the product is likely to take place) until saponification is complete. Dilute the liquid with several times its own volume of water and boil until the whole of the alcohol has been removed, adding hot water from time to time if necessary. Add dilute sulphuric acid to the solution in slight excess when the fatty acids will rise to the surface, usually as a clear oily liquid which can be separated quite readily. Finally, wash the separated acids with hot water until they are no longer acid to methyl orange and filter through a warm thick filter-paper.

In the case of drying oils these operations must be carried out as rapidly and at as low a temperature as possible, preferably in an atmosphere of carbon dioxide.

It is obvious that the above process will only yield those acids which are insoluble in water (cf. Hehner's process, page 145). In those cases where the fat gives more than a negligible Reichert value, and it is desired to examine the soluble acids, the washings should be made alkaline and evaporated to small bulk, the resulting solution again acidified, and the free fatty acids extracted with ether in the usual way. Where serious quantities of unsaponifiable matter are present, these must be removed (cf. page 120) from the soap solution before acidification.

Methods of Examination.—The methods of examination of the fatty acids are quite analogous to the same determinations on the fats themselves, and these will be described later. Such determinations may include specific gravity, melting and solidifying points, index of refraction, iodine value, etc. The only methods which have any point of difference are the determination of the mean molecular weight or neutralisation value and the determination of the anhydrides.

Mean Molecular Weight.—The neutralisation value of the fatty acids is the number of milligrams of potassium hydroxide which are required to neutralise one gram of the acids. Their mean molecular weight may then be calculated from the equation

$$M = \frac{56 \cdot 1}{n}$$

where n is the neutralisation value, and M the mean molecular weight.

Anhydrides.—Although the matter is, as yet, by no means proved, there is some evidence of the existence of anhydrides or lactones in the fatty acids separated from fats. In such cases the neutralisation value of the acids,

determined in the cold will be different from the saponification value of the acids determined in the hot. Lewkowitsch has suggested the following gravimetric method for the determination of lactones:

Five grams, or more, of the sample are dissolved in neutralised alcohol, and titrated with aqueous caustic potash. The lactone or anhydride remains unaffected as long as free fatty acid is present. The soap solution is then shaken out with ether or petroleum ether, care being taken not to dilute the soap solution too much so as to cause dissociation of the soap, when acid soaps may pass into the ethereal solution. The ethereal solution is then filtered off, the ether evaporated off, and the residue weighed. The residue must be free from ash; its neutralisation value should, of course, be nil. In this connection C. A. Browne (*J.S.C.I.*, 1915, 34, 184) has some interesting remarks. For further information see Tortelli and Pergami (*J.S.C.I.*, 1902, 21, 1187). For the general properties and preparation of anhydrides, see J. Gsell (*Analyst*, 1907, 32, 95) and Holde and his collaborators (*J.S.C.I.*, 1920, 39, 789A, 790A; 1921, 40, 817A; 1922, 41, 825A; 1923, 42, 896A; 1925, 44, B679. *Analyst*, 1921, 46, 245).

Separation of Fatty Acids

Soluble and Insoluble Acids.—The determination of the soluble and insoluble acids of fats is usually carried out where desired by the method of Hehner, described on page 145. The Reichert value is usually considered to be proportional to the amount of soluble acids present on account of the fact that in general, solubility and volatility are closely allied in the case of the fatty acids. The separation is carried out as described on page 44 above.

Solid and Liquid Acids.—It so happens that most of the saturated fatty acids are solid, whilst the unsaturated acids are liquid, so that in general, the separation of solid and liquid acids means the separation of saturated and unsaturated acids. The two notable exceptions to this rule are erucic acid, page 35, and the oleic acids formed by submitting certain fats to hydrogenation.

The Lead-salt-ether Method.—The earliest of the usual methods for separating liquid and solid acids is the lead-salt-ether method, which may be carried out in the manner recommended by Fryer and Weston:

Saponify 5 grams of the oil in the usual way. Add acetic acid till slightly in excess, and back-titrate to neutrality with alcoholic potash, using phenolphthalein as indicator. (If the mixed fatty acids are employed instead of the oil, dissolve in alcohol, and titrate with N/2 aqueous potash. Dilute with water to 100 c.c.) Distil off the alcohol on the water-bath, and dissolve the soap in 100 c.c. water. Place the solution in a 500 c.c. wide-necked, conical flask, and add slowly, with constant shaking, 200 c.c. of boiling water to which has been added 30 c.c. of 10 per cent. lead acetate solution. Fill up the flask with boiling water, and set aside to cool. When the lead salts are set and the liquid clear, pour off the latter, being careful to return any particles of lead salts which run out. Wash the salts with boiling water, shaking and cooling under the tap, meanwhile rotating so as to cause the salts to adhere to the sides of the flask. When cold, run out the wash water, and repeat the washing with boiling water. Drain the flask by turning it upside down, and remove any further moisture with a wad of cotton-wool held by the forceps. Add 200 c.c. of ether (methylated), cork the flask, and shake thoroughly; then place under a reflux condenser, and heat

on the water-bath until only a fine light suspension remains. Remove from the condenser, cork, and set aside to cool to room temperature, filter into a separating funnel, keeping the funnel covered with a large watch glass. Wash out the flask with four successive quantities of 30 c.c. of ether, pour on to filter and allow all ether to drain through. Add to the ethereal solution of soluble lead salts in the separating funnel, 100 c.c. of dilute HCl (20 c.c. conc. HCl to 100 c.c. with water), stopper the separator, and shake thoroughly to decompose the lead salts. Stand till a complete separation occurs between the ether and aqueous layers, and then run off the precipitated lead chloride and water, and wash the ethereal layer with lots of 10 c.c. water till free from mineral acid, separating well each time. Add a few granules of fused calcium chloride to the ether, and stand for an hour, then remove the stopper, and pour out the ether through neck of separator on to a filter and run the filtrate into a 200 c.c. graduated flask. Rinse out separator with two lots of ether, being careful to retain the calcium chloride and any drops of water which have separated out. Make up the ethereal solution to 200 c.c. with ether, shake, and stopper the flask. Pipette into two flasks, A and B (latter tared), 50 c.c. of the ethereal solution, and drive off the ether in a current of CO_2 on a water-bath. Continue to heat and pass in CO_2 till no further loss in weight occurs. Immediately introduce into A the requisite quantity of Wijs' iodine solution, and ascertain the iodine value. Weigh flask B.

Yield of liquid unsaturated acids = wt. of fatty acids in flask $B \times 4 \times \frac{100}{5}$ per cent. The yield of solid acids is obtained by the difference of the above figure and the yield of total insoluble fatty acids from the oil. The yield of solid acids may be directly obtained by treating the insoluble lead salts left on the filter-paper as described previously. The iodine value should be determined. The acids should give no ash on incineration, showing that the lead salt has been properly decomposed.

Various modifications have been proposed by Oudemans (*J. Prak. Chem.*, 1866, 99, 407), Kremel (*Pharm. Zentral.*, 1891, 5, 337), Rose (*J.S.C.I.*, 1887, 6, 306), Twitchell (*J. Amer. Chem. Soc.*, 1895, 17, 289), Muter and De Koningh (*Analyst*, 1889, 14, 61), Hehner (*Analyst*, 1892, 17, 181), Lewkowitsch (*J.S.C.I.*, 1890, 9, 845).

The solubilities of the lead salts of various fatty acids in ether and in petroleum ether have been studied by G. B. Neave (*Analyst*, 1912, 37, 399).

The method has been modified, by fractionally precipitating the fatty acids by means of one-tenth the full quantity of lead required, as a means of detecting rape oil (Kreis and Roth, *Analyst*, 1913, 38, 114). A. Seidenberg (*Analyst*, 1921, 46, 465) conducts the solution of the lead salts in a similar manner to his crystallisation method described on page 399, using a mixture of ether, alcohol and chloroform. E. Twitchell uses alcohol alone (*Analyst*, 1921, 46, 466). A modification using alcohol, proposed by Tortelli and Ruggeri produces, according to Lewkowitsch, liquid acids having a higher iodine value than the original method, but as in one case the residual acids had an iodine value of seventy it is obvious that some particular classes of unsaturated acids are isolated by this means. Kawase, Suda and Fukuzawa (*J. Chem. Soc. Japan*, 1921, 42, 181; *J.S.C.I.*, 1921, 40, 664A) propose an alternative method.

Petroleum spirit has been suggested as a solvent in place of ether by Twitchell (*J.S.C.I.*, 1895, 14, 515), and Lane (*J.S.C.I.*, 1907, 26, 597) found that lead ricinoleate was insoluble in this solvent, which suggests a method for the isolation of this acid. Benzene as a solvent was suggested by Farnsteiner (*J.S.C.I.*, 1898, 17, 804), but the results obtained by this method do not appear to show any improvement.

The Potassium-salt-acetone Method.—This method was apparently first suggested by Fachini and Dorta (*J.S.C.I.*, 1910, 29, 1065; 1912, 31, 397. *Analyst*, 1914, 39, 122) and used by them particularly for the separation of arachidic acid (*vide* arachis oil, page 260). Although the method was reported upon adversely by Rideal and Acland (*Analyst*, 1913, 38, 260), A. de Waele (*Analyst*, 1914, 39, 389) reports very highly upon its simplicity. The last author proceeds as follows :

About 10 grms. of the dry fatty acids are weighed into a 150 c.c. CO_2 flask, 90 c.c. of anhydrous acetone added, the solution warmed to 25°, and 10 c.c. of N/1 potassium hydroxide added in a thin stream with stirring. The flask is then corked and immersed in ice-water for three to four hours. At the end of this period complete precipitation will have occurred.

The contents of the flask are then thrown on to a 5 or 6 cm. Buchner funnel and washed with anhydrous acetone at 0° until the residue is quite colourless. The bulk of the acetone is then removed by sucking air through the filter-paper and pressing down to a solid cake by means of a spatula. The cake is then placed in a tared 150 c.c. beaker, the adhering soaps removed from the filter-paper, and the CO_2 flask washed out with a little warm dilute potash, since part of the precipitated acids exists in the free state and adheres tenaciously to the flask. The rinsings of this flask are then run into the beaker containing the bulk of the soaps, water added, the flask warmed until solution is complete, and the acids liberated in the usual way, the boiling being continued until the lower aqueous layers become transparent.

The solid acids are then filtered off as in the determination of the Hehner acids, the cake solidified by immersion in cold water, and the drained paper with its adhering acids transferred to the tared beaker and dried at 100° until of constant weight.

The liquid acids may be separated from the acetone filtrate by adding an equal volume of water, 30–50 c.c. ether, and acidifying with hydrochloric acid. The ether layer is then washed with faintly acid water, the acid assisting in the separation of the emulsion. The ethereal layer is then run off, evaporated, etc. (cf. R. H. Kerr, *J.A.O.A.C.*, 1920, 3, 435).

Meigen and Neuberger (*J.S.C.I.*, 1922, 41, 944A) were not able to obtain good results by the original method and proposed a method depending upon the use of thallous sulphate which is described below.

The Lithium-salt-acetone Method.—This method, which has been suggested by M. Tsujimoto (*J.S.C.I.*, 1920, 39, 825A), depends upon the ready solubility of the lithium salts of the highly unsaturated acids in 95 per cent. acetone by volume and the slight insolubility of the other salts in this solvent; the method is particularly useful in the examination of fish oils. The lithium salts may be prepared by neutralising an acetone solution of the acids with lithium hydroxide, using phenolphthalein as indicator or, for larger quantities, by treating an alcoholic solution of the potassium salts with lithium acetate. A later modification by Tsujimoto and Kimura (*J.S.C.I.*, 1924, 43, B62) suggests that 10 grams of the fatty acids be dissolved in 95 c.c. of acetone and neutralised with ammonia, an aqueous solution of an equivalent amount of lithium salt being then added; the resulting acetone solution should be of 95 per cent. strength. The solution is shaken for thirty minutes and cooled in ice-water for about an hour. This modification gives a somewhat lower yield, but the use of ammonia in place of potash facilitates recovery of the lithium. Later (*ibid.*, 1925, 44, B856) Toyama and Tsuchiya suggest the use of the sodium salt in suitable mixtures of acetone and water or of acetone and alcohol.

The Magnesium-soap-alcohol Method.—This method has been used by

R. H. Kerr (*J.S.C.I.*, 1916, 35, 1121) and by Thomas and Yu (*J.S.C.I.*, 1923, 42, 233A) and has been recommended by Morgan and Bowen (*J.S.C.I.*, 1924, 43, 346T). The last authors use a solution prepared by dissolving 100 grams of magnesium acetate in 200 c.c. of water, cooling, filtering and mixing with three volumes of 95 per cent. alcohol. One part of the mixed fatty acids should be added to about five parts of this solution after heating. The magnesium soaps are then allowed to crystallise over night at room temperature, filtered off and washed with water until free from magnesium chloride.

Other Methods.—David (*Analyst*, 1911, 36, 22) and P. Falciola (*Analyst*, 1911, 36, 23, 114) have based a method of separation on the fact that the ammonium salts of the solid fatty acids are insoluble in a large excess of ammonia whilst the salts of the liquid fatty acids are readily soluble (cf. table, page 29). Falciola working on a mixture of 5 grams of oleic acid and 2·5 grams each of palmitic and stearic acids states that the separated oleate was found to contain 0·20 gram of palmitate and 0·04 gram of stearate.

The use of sulphuric acid and of the Twitchell reagent (see page 14) have been proposed by Twitchell (*J.S.C.I.*, 1897, 16, 1002) and by Lanza, but no method based upon this suggestion has yet been put forward.

Meigen and Neuberger (*J.S.C.I.*, 1922, 41, 944A) have suggested the use of thallous sulphate as a reagent for the purpose. They found that a mixture of 0·502 gram of oleic acid with 0·505 gram of stearic acid gave 0·509 gram of solid acids of iodine value 0·3 and M.Pt. 68°, while a mixture of 0·200 gram of oleic acid and 0·502 gram of stearic acid gave 0·529 gram of solid acids of iodine value 0·9 and M.Pt. 67·5°. This reagent has been used by Holde, Selim and Bleyberg (*J.S.C.I.*, 1924, 43, B755, B916), who find that 100 grams of water dissolve 0·0461 gram of thallous oleate at 15° and 0·3034 gram at 80°; 100 grams of 50 per cent. alcohol (by volume) dissolve 0·9247 gram at 15° and 100 grams of 96 per cent. alcohol (by volume) dissolve 2·254 grams at 15°. They use the following method :

1 gram of the mixed fatty acids is dissolved in 50 c.c. of 96 per cent. alcohol, neutralised with N/2 or N/10 alcoholic potassium hydroxide diluted with the same solvent to 125 c.c. and 65 c.c. of water and 35 c.c. of 4 per cent. thallous sulphate solution are added at the ordinary temperature. The thallous salts of the solid acids are separated by filtration through a fluted filter, and after washing, the free fatty acids are liberated from the precipitate and the filtrate by means of sulphuric acid, and determined gravimetrically after removal of the solvent.

Grün and Janko (*J.S.C.I.*, 1922, 41, 21A) have suggested a method, which depends on the wide difference in boiling-point of the mixed esters of the saturated fatty acids and of the bromine addition products of the esters of the unsaturated acids. The esters are prepared in the usual way with 1–2 per cent. alcoholic sulphuric or hydrochloric acid. The bromination is carried out by saturating the chloroform or carbon tetrachloride solution with bromine. The product is freed from the solvent and washed with sodium bicarbonate solution. The distillation is best carried out at 2–4 mm. pressure. The ethyl esters of the saturated fatty acids distil over up to 175°, the decomposition of the brominated esters not beginning until 190°. The bromine is removed from the residual brominated esters by boiling for several hours with alcoholic hydrochloric acid (2N–3N) and granulated zinc, which must be pure and have a large surface. The same weight of zinc should be used as that of the brominated esters. The alcohol, hydrochloric acid, and salts are removed by pouring into water, and the esters extracted with ether, which is distilled off. The method gave very exact results on known mixtures. If more than 90 per cent. of unsaturated acids are present (as shown

by the iodine value) an equal weight of ethyl stearate is added to the mixed esters before distillation and the addition allowed for in the calculation. D. Holde (*ibid.*, 1925, 44, B250) has found that the method cannot be applied to the case of the fatty acids from arachis oil, as ethyl arachidate and lignocerate boil, under 2 mm. pressure, above the decomposition temperature (190°) of ethyl dibromostearate, whilst ethyl tetrabromostearate, derived from the linolic acid (7–8 per cent.) present in arachis oil, decomposes at a considerably lower temperature.

Treatment of the zinc salts with carbon bisulphide has been recommended by Sear, and with ether by Jean and by Bömer.

The Method Recommended.—The reports of various observers differ widely as to the relative utility of the different processes suggested. At the present time it would appear that no great advances have been definitely made on the original lead-salt-ether method, and it must be emphasised here that it has not yet been found possible to effect a complete separation as judged by a zero iodine value for the saturated acids. The thallous-sulphate method certainly looks promising, but it requires considerably more examination before a final opinion can be given. It would be a most useful piece of work for the various methods to be compared with particular reference to the thallous-sulphate method. A further point which should be mentioned is that the utility of any particular method will depend to a considerable extent on the actual fatty acids present.

Isolation of Individual Acids

It must be stated at the outset that the isolation of individual fatty acids in a state of purity from such mixtures as occur naturally in fats is extremely difficult and laborious and that their quantitative determination to any high degree of accuracy under all conditions is impossible. In spite of this statement, however, the isolation and approximate determination of many of the more common acids can be carried out and the results can, in many cases, be accepted.

Solid Acids.—One of the earliest attempts to bring about such a separation was that of Heintz (*J. Prakt. Chem.*, 1855, 66, 1) who precipitated the alcoholic solution of the mixed solid acids with alcoholic solutions of barium or magnesium acetate. The usual method is to add sufficient of the reagent to combine with, say a tenth of the fatty acids present, and filter off the precipitate formed. A further quantity of the reagent is then added after the solution has been neutralised with ammonia, the further precipitate filtered off, and so on until no further precipitation takes place. As a general rule the salts of the higher fatty acids separate first (cf. Morgan and Bowen, *J.S.C.I.*, 1924, 43, 346T). Lead and lithium, particularly the latter (*vide* E. V. Walker, *J.C.S.*, 1923, 123, 2837), have also been used in a similar manner, whilst Edelstein (*J.S.C.I.*, 1912, 31, 730) has suggested the separation of the volatile acids by fractional precipitation with silver nitrate. Cf. J. Gsell, *Analyst*, 1907, 32, 95; Heiduschka and Ripper, *J.S.C.I.*, 1924, 43, B184; Hodgson and Keane and Narracott, *Analyst*, 1909, 34, 435, 436; E. B. Holland, *J.S.C.I.*, 1911, 30, 433; Langheld and Zeileis, *Analyst*, 1913, 38, 273; H. Agulhon, *Analyst*, 1913, 38, 274.

Various suggestions have been made concerning the isolation and determination of individual acids which will be mentioned below under the acids themselves.

Liquid Acids.—Various unsaturated acids may be present in the liquid acids. Their degree of unsaturation will be indicated to a considerable extent by the iodine value. The iodine value of oleic acid is 90, whilst that of linolenic is 274; it will be possible therefore in those cases where

these two acids only are present to calculate the respective quantities from the iodine value of the mixture. Where a large number of unsaturated acids are present, which is, of course, always a possibility, the problem is more complicated and special methods are necessary. The earliest work on this subject was carried out by Hazura (*Monat. f. Chem.*, 1887, 8, 147, 156, 260; 1888, 9, 180, 190; 469, 478, 944, 947; 1889, 10, 190) by oxidation and isolation of the products, and by the preparation of the bromine addition compounds and separation of these by their different solubilities. The result of the work of Hazura and his collaborators served to show that when unsaturated fatty acids are oxidised by means of a dilute aqueous solution of potassium permanganate hydroxyl groups are added equivalent in number to the unsaturated valencies in the molecule, that is each double bond will produce two, and also that the hydroxylated product contains the same number of carbon atoms as the original acids. In this way oleic acid produces dihydroxystearic acid, linoleic acid produces sativic or tetrahydroxystearic acid and linolenic acid produces linusic or hexahydroxystearic acid. The clupanodonic acid of fish oils appears to offer an exception to this rule as it is broken down into simpler compounds. The experimental methods of Hazura are described by Lewkowitsch in the following way:

" 30 grms. of liquid fatty acids are neutralised with 33 c.c. of caustic potash of 1·27 specific gravity. The resulting soap is dissolved in 2000 c.c. of water, and an equal volume of a 1½ per cent. solution of potassium permanganate is added in a thin stream with constant stirring. The solution is allowed to stand for ten minutes, and as much of a sulphurous acid solution added, with continuous agitation, as will dissolve all the precipitated hydrated manganese peroxide, and impart to the solution an acid reaction. Dihydroxystearic and sativic acids are precipitated (A), whereas linusic and isolinusic acids remain dissolved (B).

" The precipitated acids (A) are first washed with a little ether, in order to remove some of the original liquid acids that have escaped oxidation, and then extracted with large quantities of ether at the ordinary temperature, 2000 c.c. of ether being used for every 20 grams of the precipitate. The ethereal solution, containing dihydroxystearic acid, is evaporated down to 150 c.c.; on cooling crystals are obtained which, after recrystallisation from alcohol, can be identified as dihydroxystearic acid by their *habitus*, melting-point, molecular weight and acetyl value. The portion which is found to be insoluble in the cold ether is boiled out repeatedly with large quantities of water. Each quantity is filtered off hot and allowed to deposit crystals on cooling. Each crop of crystals is examined separately. Sativic acid can be identified by its melting-point and crystalline form. Any insoluble acid represents dihydroxystearic acid which had not been dissolved by ether.

" The acid filtrate (B) is neutralised with caustic potash, boiled down to one-twelfth or one-fourteenth of its original volume, and acidulated with sulphuric acid. The precipitate, consisting of a brown flocculent mass, is dried by exposure to the air, and treated with ether, which dissolves azelaic acid and other secondary acidic products of oxidation. The insoluble portion is then crystallised, first from alcohol and then from water. Isolinusic and linusic acids are recognised by their melting-points and crystalline forms: isolinusic acid presents under the microscope characteristic needles and linusic acid obtruncated rhombic plates. To effect a separation of the more soluble isolinusic acid from the less soluble linusic acid, the mass is recrystallised from a moderate quantity of water. By weighing the several acids thus obtained, the quantitative composition of the liquid acids may be estimated approximately."

It must be borne in mind that these methods have little quantitative significance, and are chiefly of value for detecting the constituents of a mixture. Modifications of the methods have been suggested by Fahrion, Farnsteiner and other workers, but no great improvements on the original work have been made; as has been already stated the whole problem of the investigation of mixtures of fatty acids needs re-investigation on a large scale.

A further method which may be used for the separation and isolation of the unsaturated acids depends upon the differences in the properties of their bromine derivatives. When oils are brominated, as described under the insoluble bromide value, dibromides are produced from oleic acid, tetrabromides from linoleic acid, hexabromides from linolenic acid, and octobromides from the highly unsaturated acids of fish oils. Under the conditions of the experiment dibromides and tetrabromides are soluble, whilst the hexabromides and octobromides are insoluble and can be filtered off. Hexabromides are usually obtainable in a crystallisable condition, which melt to a clear liquid at about 180°—the octobromides on the other hand yield plastic precipitates which are difficult to filter, and which darken at about 200°, and decompose without fusing. Mixtures of hexabromides and octobromides can be separated by means of boiling benzene, Lewkowitsch having shown that the hexabromide separated from octobromide by means of benzene exhibits no trace of blackening when heated to its melting-point.

Further yields of hexabromide and octobromide can frequently be obtained by slight concentration of the solution, but as a rule the M.Pts. are lower. When these have been removed—their amount may be reduced to a minimum by the use of small amounts of acetic acid and low temperatures—the mother liquors still contain the di- and tetrabromides. The concentrated ethereal solution may be evaporated, washed with sodium thiosulphate solution to remove iodine, and evaporated to dryness. The residue is just dissolved in boiling petroleum ether (B.Pt. 40°–60°) and allowed to crystallise when practically the whole of the tetrabromide is deposited, the dibromide remaining in solution.

Grün and Janko (*J.S.C.I.*, 1922, 41, 21A) suggest the preparation of the ethyl esters, and the bromination of these in carbon tetrachloride solution. The brominated esters are then distilled under 4 mm. pressure, when those of the saturated acids distil over up to 175°.

The Method of Alcoholysis

This method—which depends upon the fractional distillation of the methyl or ethyl esters of the fatty acids—has been extensively used by various workers for the resolution of complex mixtures of fatty acids into their constituents. It was originally described by A. Haller (*Analyst*, 1907, 32, 52) who used it to determine the constitution of coconut oil, castor oil, linseed oil, etc. (*Analyst*, 1907, 32, 53; *J.S.C.I.*, 1908, 27, 234; 1907, 26, 328), but the same idea had been suggested previously by Fox and Wanklyn, who, a number of years before (*Analyst*, 1884, 9, 73), described a process for the examination of butter fat, which depended upon the formation of ethyl butyrate on heating with alcoholic potash. The method has been used by a large number of workers for various products. A list of the more important is given here:

Henriques. "The Ethyl Esters of the Fatty Acids of Almond Oil." *Zeit. Angew. Chem.*, 1898, 15, 338.

H. Bull. "The Alcoholysis of Cod-Liver Oil." *Analyst*, 1907, 32, 25.

Meyer. "The Alcoholysis of Cotton-Seed Oil." *Chem. Zeit.*, 1907, 31, 793.
Fourwan and Piettre. "The Determination of the Composition of Complex Lipoids by Alcoholysis." *Analyst*, 1912, 37, 463.
Smedley. "The Composition of Butter Fat." *Biochem. J.*, 1912, 6, 451.
G. D. Elsdon. "Alcoholysis and the Composition of Coconut Oil." *Analyst*, 1913, 38, 8.
G. D. Elsdon. "The Composition of Palm-Kernel Oil." *Analyst*, 1914, 39, 78.
M. Tsujimoto. "The alcoholysis (Incomplete) of Japanese Sardine Oil and Herring Oil." *J.S.C.I.*, 1913, 32, 96.
Holland, Reed and Buckley. "Improved Methods for Fat Analysis." *Analyst*, 1916, 41, 252.
Crowther and Hynd. "The Fatty Acids of Milk Fat." *Biochem. J.*, 1917, 11, 139.
Holland and Buckley. "The Composition of Butter Fat." *Analyst*, 1918, 43, 269.
A. Grun. "The Use of Esters for the Determination of the Acetyl Values." *Analyst*, 1920, 45, 105.
Jamieson, Baughman and Brauns. "The Composition of Arachis Oil." *Analyst*, 1921, 46, 457.
Holde and Wilke. "The Alcoholysis of Colza Oil." *J.S.C.I.*, 1922, 41, 598A.
G. A. Perkins. "The Preparation of the Ethyl Esters of Chaulmoogra and Cod-Liver Oils." *J.S.C.I.*, 1922, 41, 996A.
Holland and Buckley. "The Composition of Butter Fat." *Analyst*, 1923, 48, 555.
A. André. "The Alcoholysis of Grape-Seed Oil." *Analyst*, 1923, 48, 290.
A. André. "The Separation of Methyl oleate and Methyl linoleate." *J.S.C.I.*, 1923, 42, 364A.
A. Marcan. "The Use of the Ethyl Esters of Chaulmoogra Oil." *Analyst*, 1924, 49, 88.
Milligan, Knuth and Richardson. "The Alcoholysis of Whale Oil." *Analyst*, 1924, 49, 149.
Jamieson and Baughman. "Alcoholysis of Sesame Oil." *Analyst*, 1924, 49, 236.
G. A. Perkins. "Alcoholysis of Oils of the Chaulmoogra Series." *Analyst*, 1924, 49, 236.
Channon, Drummond and Golding. "The Variation in the Composition of Butter Fat." *Analyst*, 1924, 49, 311.
G. D. Elsdon. "The Composition of Coconut Oil." *Analyst*, 1924, 49, 274.
G. D. Elsdon. "Alcoholysis and the Composition of Oils and Fats." *Analyst*, 1924, 49, 423.
W. N. Stokoe. "The Composition of Coconut Oil." *Analyst*, 1924, 49, 577.
John Allan. "The Composition of Coconut Oil." *Analyst*, 1925, 50, 16.
Armstrong, Allan and Moore. "The Fatty Acid Constituents of Some Natural Fats." *J.S.C.I.*, 1925, 44, 63T.

The experimental method now used is essentially that originally suggested by Haller, but a number of details have been introduced with the idea of

removing some of the more obvious errors of the process and of obtaining roughly quantitative methods. The experimental details of the process of Crowther and Hynd in their work on butter fat are given below in detail, as they were a distinct improvement on those generally adopted up to that time.

" 136·11 g. clarified fat were weighed off accurately into a round-bottomed litre flask and mixed with 214 c.c. absolute methyl alcohol containing 2·5 per cent. hydrogen chloride, and 323 c.c. pure dry ether. The flask used was fitted to a fairly long double-surface condenser by means of a ground-glass joint, and the condenser carried a delivery tube, which was bent twice at right angles, and led into a series of U-tubes, surrounded by a freezing mixture of ice and salt. The esterification mixture was then heated for twelve hours on a water-bath at a temperature just sufficient to keep the liquid refluxing gently. After allowing to cool thoroughly, the U-tubes were detached, and the small quantity of liquid (10 to 15 c.c.), which had collected, transferred to a litre graduated flask (A). The tubes were washed out with a little pure dry ether, and the washings also added to flask (A). The liquid, which had collected in these tubes, was mainly ether, but at the same time an appreciable quantity of methyl ester (methyl butyrate) was always found to be present. Consequently, if this precaution was not taken, loss of this ester resulted.

" To the ether-alcoholic solution of esters in the reaction flask slightly more than the calculated amount of barium carbonate was added to remove the free hydrogen chloride. Though the mixture was frequently shaken, neutralisation proceeded slowly, but finally all the mineral acid was removed as indicated by Congo paper. The flask was then fitted with a five-pear still head and the ether and methyl alcohol distilled off, using a long double-surface condenser, and collecting the distillate in a flask cooled in a freezing mixture. The distillate, which contained in addition to ether and alcohol the greater part of the butyric ester, was then transferred to flask (A), the collection flask being washed out with ether, and the washings also added to (A). The residue, which consisted of methyl esters, glycerol, barium chloride, the excess of barium carbonate used, and the traces of solvents, was transferred by means of ether to a separating funnel and shaken with brine. This caused the ethereal solution of esters to separate out on top free from glycerol which was held in the salt solution. The process was repeated three times, and the separated ethereal solution then dried over anhydrous freshly ignited magnesium sulphate. After standing over night the magnesium sulphate was filtered off through a large Gooch crucible prepared in the usual way, and washed well with dry ether."

Fractional Distillation of Esters.—A 250 c.c. Claisen distilling flask was fitted with a dropping funnel and thermometer, a portion of the dried ethereal solution of esters introduced through the funnel, and the ether distilled off carefully on the water-bath, the distillate being again collected in a cooled receiver, so as to avoid any loss of esters. As the ether evaporated, more solution was added by means of the tap-funnel until the whole had been introduced, and finally the flask and funnel were washed with pure dry ether. When all the ether had been distilled off, the receiver was removed, its contents transferred to flask (A), and in its place was fitted a " Perkin fractionation triangle." The tap-funnel was removed from the straight neck of the Claisen flask, which was now fitted with a cork, carrying a tube drawn out to a *very* fine capillary, and reaching to the bottom of the flask. The distillation of the esters was then carried out, at first at ordinary pressure, and then in *vacuo*, the distilling flask being heated by means of an asbestos air-bath. After

the fraction boiling about 140/15 mm. had been collected the condenser was dispensed with, and the residual esters transferred with ether to a smaller Claisen flask, the side limb of which was connected directly with the receiver.

The first fraction that distilled over consisted mainly of ether, and consequently was added to the litre flask (A), which contained all the solvent alcohol and ether recovered from the process. The volume of this was now made up to the mark with pure alcohol (or ether) and the amount of methyl ester in solution determined as described below.

It was found that, as a rule, the fractionation must be repeated three or four times before a sufficient separation was effected. Appended are the details of the final (third) fractionation in the experiment described :

TABLE X.—FRACTIONAL DISTILLATION OF ESTERS

Fraction.	Temperature. °C.	Pressure. mm.	Weight. g.
1	65–130	Atmospheric	1·6690
	–150	Atmospheric	
2	53– 75	15	1·9662
3	–110	15	1·3396
4	–135	15	1·0886
5	–155	15	2·4600
6	–185	15	14·1852
	–200	15	
7	184–190	13	18·3872
8	–197	13	18·1542
9	–202	13	18·1230
10	–202	12	16·7630
11	–206	12	18·6558
12	–211	12	10·0762
13 (residue)	..	..	6·7827
Total weight of fractions			129·6507

The temperatures quoted for the various fractions indicate the points at which the first and last drops contained in the respective fractions came over.

On comparison it will be seen that the boiling-points given on p. 21 fall between these temperatures, and that it was about these points that the bulk of the fraction distilled. For example, in the above fractionation fraction 3 corresponds to (*d*) on p. 140, fraction 5 to (*f*), fractions 7 to 11 (inclusive) to (*h*). The collection of the last named in five fractions was necessitated simply by the relatively large volume of distillate obtained at this stage, collection-tubes of uniform size being used for general convenience.

Determination of Methyl Butyrate Volatilised with Solvents.—A 250 c.c. conical flask was fitted with a cork carrying a dropping funnel and a delivery tube, the latter being connected with a condenser. 20 c.c. of alcoholic KOH solution (roughly N/2) were transferred to the flask and 100 c.c. of the ether-alcoholic solution from flask (A) placed in the funnel, the stem of which, drawn out to deliver small drops, reached almost to the surface of the potash solution. The flask was then heated on the water-bath, and the ether-alcoholic solution allowed to drop in slowly, so that the volume in the flask remained about the same. When all the solution had been added the distillate was transferred to the funnel, and the distillation repeated. All

the ester in the original solution was thus hydrolysed, and after cooling the contents of the flask a few drops of phenolphthalein were added, and the excess of potash titrated with standard (roughly N/2) hydrochloric acid.

A blank experiment was carried out at the same time, using a mixture of 50 c.c. pure ether and 50 c.c. neutral alcohol in place of the ether-alcoholic solution of ester, and proceeding exactly as described above. From the difference between the two litres the amount of ester can be calculated if the reasonable assumption be made, that it consists solely of methyl butyrate. In all cases the mean of two closely-agreeing determinations was used in calculating the results.

Appended are the details for the analysis here described :

	c.c. HCl (N/1 × 0·497) required.	
	a	*b*
Blank experiment . . .	31·89	31·86
100 c.c. ester soln. . . .	21·05	21·00
Difference	10·84	10·86
Mean litre	10·85 c.c.	

Hence weight of methyl butyrate in solution (1000 c.c.)

$$= 10{\cdot}85 \times 10 \times 0{\cdot}497 \times 0{\cdot}1021 \text{ g.}$$
$$= 5{\cdot}507 \text{ g.}$$

If this weight be now added to the 129·651 g. of esters obtained in the fractionation, a total of 135·158 g. of esters is arrived at as having been obtained from 136·11 g. of butter fat.

The various fractions obtained were then examined for their iodine and saponification value from which values the proportion of each of the esters present in each fraction, is calculated on the assumption that only three are present, one of which is methyl oleate. Crowther and Hynd prepared an artificial mixture of fatty acids similar to that prepared from butter fat and subjected this mixture to alcoholysis calculating the amounts of the various acids present by the method suggested above.

TABLE XI.—ALCOHOLYSIS OF FATTY ACIDS (CROWTHER AND HYND)

Acid.	Wt. of Esters cal. from Wt. of Acid taken.	Wt. of Esters found by Analysis.
	g.	g.
Butyric	5·03	5·026
Caproic	1·89	1·854
Caprylic	1·21	1·240
Capric	1·41	1·467
Lauric	4·06	3·994
Myristic	21·76	22·108
Palmitic	15·30	14·950
Stearic	1·32	1·416
Dihydroxystearic . . .	..	0·210 *
Oleic	41·98	41·675
Total weight . .	93·96 g.	93·940 g.

* 0·21 g. Dihydroxystearic ester would be produced from 0·188 g. oleic ester, therefore total weight of methyl oleate found=41·863 g.

These results are really remarkable, they would appear to be a complete vindication of the process, and yet it is difficult to understand how oleic acid can be present in the first fractions and yet stearic acid be absent in all fractions below the palmitic. The question has been discussed at length by Channon, Drummond and Golding (*Analyst*, 1924, 49, 311), G. D. Elsdon (*ibid.*, 1924, 49, 423), W. N. Stokoe (*ibid.*, 1924, 49, 577), and John Allan (*ibid.*, 1925, 50, 16).

The question has been quite recently considered at length by Armstrong, Allan and Moore (*J.S.C.I.*, 1925, 44, 63T), who consider that the capricious results obtained and the adverse opinions passed by previous workers are due to the fact that insufficient attention has been paid to the fractionation. They state that it is quite possible so to continue this that every alternate fraction consists of a pure ester whilst the intermediate fractions will consist of mixtures of two esters, but they do not state how many times it is necessary to refractionate in order to arrive at this condition.

The method used by these authors is likely to form the basis of further work on the subject, so that it is included here *in extenso*.

" A quantity of the oil under examination, varying from 400 to 1000 g. or more, according to the anticipated complexity of the mixture of acids present, is saponified by means of alcoholic potash, and from the resulting potash soaps the fatty acids are obtained in the usual manner. The fatty acids so obtained are examined to determine their mean molecular weight (saponification equivalent), and iodine value. On the iodine value depends which of the following procedures is adopted:

" 1. Should the fatty acids have a low iodine value, say below 20, as in the case of the nut oils, they are esterified (see below), and the esters fractionally distilled. By this means a fraction (or fractions) is obtained of high iodine value, which is more conveniently examined for the nature of the liquid acids, and admits more readily of their separation, than would the original mixture of acids.

" 2. In the case of a hard fat having an iodine value of say 20–45, the fatty acids are recrystallised from 70 per cent. aqueous alcohol until they are separated into two portions—one, the solid acids, of which the iodine value will have been reduced to 2 or 3, and the other a fraction containing practically all the liquid acids together with some of the solid acids. This fraction of high iodine value is then separated into its solid and liquid acids by means of the Gusserow-Varrentrapp method. The solid and liquid acids so obtained are then separately esterified and the esters examined as described below.

" 3. In the case of soft fats, such as greases, palm oils, and liquid oils, the whole mixture of fatty acids is submitted to the Gusserow-Varrentrapp (lead-salt-ether) process, and the resulting solid and liquid acids are separately esterified and the esters examined as described below.

" When using the Gusserow-Varrentrapp method the solid acids are generally left contaminated with liquid acids, and in consequence may show an appreciable iodine value. In such cases they are crystallised from 70 per cent. aqueous alcohol before esterifying, and the small quantity of acids remaining in the alcoholic solution is again submitted to the Gusserow-Varrentrapp separation.

" The esterification of the acids is carried out as follows: A quantity (500 g.) of the fatty acids is dissolved in 1500 g. of absolute alcohol, and to the solution there are added 150 g. of concentrated sulphuric acid. In the case of liquid acids 100 g. of sulphuric acid will be desirable. After boiling

for about three hours the mixture is allowed to cool and the supernatant layer of esters separated. The alcoholic liquor is then concentrated to about half its original volume, cooled, poured into water, and the esters are collected by extraction with petrol ether. The petrol ether solution and the previously separated esters are united and the solution is washed, first with water to remove alcohol and mineral acid, and subsequently with aqueous soda solution to remove any free fatty acids. (Such free fatty acids should be recovered from their sodium salts, esterified, and united with the bulk.)

" On removing the solvent the ethyl esters are obtained as a light brown liquid which, after distilling under reduced pressure, forms a colourless liquid or semi-crystalline mass, agreeing very closely in mean molecular weight (saponification equivalent) and iodine value with the theoretical figures for the ethyl esters of the original fatty acids. Since the war really pure methyl alcohol has been difficult to procure (this would not appear to be necessary) hence the use of ethyl alcohol. Under no circumstances do we use the Haller method of alcoholysis. We consider this method to be quite unsuitable for the preparation of pure esters, as there is no means of separating the unchanged glycerides which are always present.

" The fractional distillation of the esters is, of course, carried out under reduced pressure. For the last twelve years we have used Pfeiffer-oil pumps of considerable capacity. These, when well tended, will maintain a pressure of 3-5 mm. for hours on end—a great help where constancy of pressure is indispensable.

" The distillation flasks are a modification of what are known as Ladenburg distillation flasks. They vary in capacity from 50 to 500 c.c., and are provided with a two-bulbed neck, which, when packed with glass Raschig rings, forms a fractionating column $6\frac{1}{2}$ to 7 in. high. These flasks were introduced and largely used by R. Willstätter, and are very efficient.

" Distillation should proceed at the rate of twenty small drops per minute."

As a result of such an investigation in the case of coconut oil, they obtained 718 grams of ethyl esters, from which the following fractions were ultimately obtained.

Table XII.—Fractional Distillation of Ethyl Esters from Coconut Oil

Fraction.	B.P. (3·5 mm.). °C.	Weight. g.	Sap. Equiv.	Iodine Value.
No. 1	51	51	171·5	Nil.
2	51–70	18	172·9	,,
3	70–71	27	199·7	,,
4	71–100	35	224·7	,,
5	100–102	231	227·6	,,
6	102–121	128	233·2	,,
7	121–123	81	256·2	0·3
8	>123	147	289·1	30·2

It will be observed that the iodine values of the various fractions are quite different in proportion from those obtained by Crowther and Hynd (v.s.).

Further work on this subject is desirable. It may be that along these

lines a method of separating fatty acids may be devised, but it is bound to be laborious, and in its present form can never become a routine laboratory method.

The Duclaux Method.—This method (*Ann. Chim. Phys.*, 1874, 2, 289) was designed to determine the proportions of a mixture of volatile fatty acids by means of the determination of the rate at which they distil from an aqueous solution. The method has been studied at length by H. D. Richmond (*Analyst*, 1908, 33, 209, 305; 1917, 42, 125, 133; 1919, 44, 255); Upson, Plum and Schott (*ibid.*, 1917, 42, 214); A. R. Lamb (*ibid.*, 1917, 42, 214); D. C. Dyer (*J.S.C.I.*, 1917, 36, 236); Bockhout and de Vries (*Analyst*, 1917, 42, 149); Gillespie and Walters (*ibid.*, 1917, 42, 389); Reilly and Hickinbottom (*J.S.C.I.*, 1919, 38, 913A); Wiegner and Magasanik (*Analyst*, 1920, 45, 24); and W. Arnold (*J.S.C.I.*, 1922, 41, 181A). The most thorough investigation of the subject is that by Richmond (*Analyst*, 1919, 44, 255), where lengthy tables are given for the distillation constants of the acids from formic acid to caproic acid. This paper should be consulted by all those interested in the subject.

Individual Acids

Acetic Acid.—The following method is proposed by R.D. Crowell (*Analyst*, 1918, 43, 172) for the separation of acetic, propionic and butyric acids:

Fifty c.c. of the solution are measured out into a precipitating jar, 2·5 c.c. of 50 per cent. sulphuric acid are added, and sufficient solid silver sulphate to precipitate all the chlorides present. The mixture is stirred with an electric stirrer, and should show, on testing, an excess of silver. It is filtered and 25 c.c. of the filtrate are distilled with 20 c.c. of 33 per cent. phosphoric acid in the usual manner for total volatile acids. Distillation is carried on until the residue amounts to 20 c.c., and repeated three times with the addition of 20 c.c. of carbon dioxide-free water each time. The distillate is titrated with N/4 sodium hydroxide, and the neutral liquid boiled down to about 8 c.c. and transferred to a tared weighing-bottle, in which it is evaporated to dryness on the steam-bath, and then dried at 220° for twelve hours and weighed. The total acidity, expressed as sodium acetate, subtracted from the total salt weight, gives the weight of total CH_2 groups, which, multiplied by 4·2, gives the quantity per 100 c.c. of the sample solution. Another portion of the standard solution (150 c.c.) is treated as before for the removal of chlorides; 100 c.c. of the filtrate are distilled with 20 c.c. of phosphoric acid, as before, for total volatile acids. The distillate is titrated with N/4 barium hydroxide, and the solution is evaporated to a volume of 5–8 c.c. The concentrated liquid is then acidified with N/4 hydrochloric acid equivalent to the titration value. The acid liquid is transferred to a 300 c.c. separating funnel, and the flask rinsed out with two portions of 25 c.c. of the salting solution and two portions of 25 c.c. each of filtered kerosene. On thorough shaking, the butyric acid, together with some of the propionic, enters the kerosene layer. The salt solution is drawn off and the kerosene washed with a further 10 c.c. of salt solution. The kerosene in the separating funnel is treated with 150 c.c. of carbon dioxide-free water, and the whole is titrated with N/4 barium hydroxide with frequent shaking. At the neutral point, the aqueous solution is drawn off into a 250 c.c. flask and diluted to the mark with washings of the kerosene. The whole solution is treated with 12·5 c.c. of 50 per cent. sulphuric acid and 3 grams of solid silver sulphate, and 200 c.c. are distilled with 40 c.c. of phosphoric acid for volatile acids as before. The distillate, titrated with N/4 sodium hydroxide, is evaporated and the sodium salts are dried at 200 C. as before. The sodium propionate equivalent of the titration value,

subtracted from the salt weight, gives the weight of CH_2 groups present as butyric acid in the distillate. This value, calculated in terms of 100 c.c. of the standard sample, has to be corrected by a factor F determined by the analysis of known mixtures, the average value of F being 1·120. The corrected value for CH_2 groups due to butyric acid, subtracted from the total CH_2 groups found in the first operation, gives the CH_2 groups due to propionic acid, and the acetic acid is found by the difference between the total volatile activity and the combined butyric and propionic equivalents.

This method is said to give useful results, having an accuracy of 3 to 4 per cent. (cf. also butyric acid below).

Acetic acid has not definitely been discovered in natural fats, but the following observers report some evidence in this direction. K. Bhaduri (*J.S.C.I.*, 1914, 33, 266) in the oil of *Argemone Mexicana*, Dunbar and Binnewies (*ibid.*, 1920, 39, 346A), in the oil of the proso millet, and A. W. Knapp (*ibid.*, 1923, 42, 508A) in cacao butter, in addition to earlier observations by other workers.

Butyric Acid.—This acid may be separated from propionic and acetic acids as described under acetic acid above. According to A. Lasserre (*Analyst*, 1908, 33, 133) acetic and formic acids may be separated from butyric and valeric acids by extracting the aqueous solution of the mixed acids with benzene, in which only the last-named acid dissolves, and from which they may be recovered by treatment with baryta. This method has been studied by T. R. Hodgson (*ibid.*, 1909, 34, 435), and by Keane and Narracott (*ibid.*, 1909, 34, 436). Hodgson finds that the best results are obtained when a volume of benzene is employed equal to twice that of the volume of the acid solution to be extracted; under these conditions he finds that although it cannot lay claim to any high degree of accuracy, yet useful results can be obtained in many cases. Keane and Narracott, on the other hand, find that the method does not rest upon a satisfactory basis and that considerable variations are likely to be obtained.

Phelps and Palmer (*J.S.C.I.*, 1917, 36, 567) have devised a method for the separation of butyric acid from formic and acetic acids by the solubility of the quinine salts in carbon tetrachloride. The solution containing the three acids is neutralised with barium hydroxide solution, a quantity of quinine sulphate sufficient to precipitate the barium is added, the barium sulphate is separated by filtration, and the filtrate is evaporated under reduced pressure; the residue obtained is then extracted with carbon tetrachloride and the quinine butyrate recovered by evaporating the solvent. From 89·7 to 100·5 per cent. of the butyric acid present is found by the process. The solubilities of quinine butyrate and quinine propionate are so nearly alike that only a partial separation of these two salts can be effected, but the propionate may be separated readily from the formate. The M.Pts. and solubilities of the quinine salts mentioned are as follows :

TABLE XIII.—MELTING-POINTS AND SOLUBILITIES OF QUININE SALTS

	M.Pt. °C.	Solubility in Carbon Tetrachloride.
Quinine formate . .	110·0–113·0	1 in 16,000
,, acetate . . .	124·0–126·0	1 ,, 2,000
,, propionate .	110·5–111·0	1 ,, 450
,, butyrate . .	77·5	1 ,, 25
,, sulphate . .	214·0	1 ,, 40,000

E. Fyleman (*ibid.*, 1924, 43, 142T) has suggested a method for the determination of butyric acid in the presence of acetic acid by its selective oxidation by means of potassium dichromate solution in sulphuric acid of a definite strength.

A test for butyric acid, which depends upon the development of a pink colour on treating a dilute solution of butyric acid with hydrogen peroxide in the presence of ferrous iron, and, after the removal of the iron, adding sodium nitroprusside and acidifying, has been suggested by G. Denigès (*Analyst*, 1918, 43, 145). Although this reaction is not given by acetic acid it has been shown by F. Bamford (*ibid.*, 1924, 49, 226) that both caproic and caprylic acid give the same colour and that the test is not specific for butyric acid.

Butyric acid occurs, to a considerable extent, in butter, whilst O. von Friedrichs (*J.S.C.I.*, 1920, 39, 304A) states that it occurs to the extent of 0·14 per cent. in fir-seed oil.

The action of butyric acid on aluminium is discussed by Seligman and Williams (*J.S.C.I.*, 1916, 35, 88), whilst the viscosity has been studied by A. E. Dunstan (*J.C.S.*, 1915, 107, 667).

Caproic, Caprylic and Capric Acids.—The separation of these acids has been considered by Gsell (*Analyst*, 1907, 32, 95) who bases a method on the formation of the anhydrides. Lewkowitsch, however (*J.C.S., Proc.* 1890, 91), considers that this method is unreliable and further work is desirable to decide between these two opinions. A useful method for the separation of these acids is that by fractional precipitation of the lithium salts already mentioned on page 49 above.

Lauric and Myristic Acids.—The separation of these acids has been studied by Jacobson and Holmes (*J.S.C.I.*, 1916, 35, 696), who devised a method for the separation of lauric acid when present in a mixture of myristic, palmitic and stearic acids and a method for the separation of myristic acid from a mixture in which it occurs together with palmitic and stearic acids. They describe a separation of the former in the following way :

" A mixture of 0·5 grm. of each of the four acids was converted into potassium soaps and, after evaporating off the alcohol, was taken up in 400 c.c. of water and precipitated with a slight excess of lithium acetate solution. In this case the precipitated lithium salts weighed 1·562 grms. equivalent to 1·527 grms. of acid mixture, which was 76·3 per cent. of the original acid mixture, whereas 75 per cent. should have been obtained if the separation had been perfect.

" The filtrate was concentrated to one-half its volume, cooled, and filtered, yielding a precipitate weighing 0·208 grm., and the acid obtained from this precipitate yielded a neutralisation value of 278·3, and had a melting-point of 43·2°, whereas the acid obtained by evaporating the filtrate to dryness gave a neutralisation value of 271·2 and the same melting-point. Calculated for lauric acid: 280·5 and 43·6° respectively.

" The water-insoluble salts from this separation yielded an acid mixture having a neutralisation value of 217·5, whereas a mixture of equal quantities of myristic, palmitic and stearic acids gives a neutralisation value of 220·9."

Whilst the second they carry out as follows :

" 0·5 grm. each of magnesium myristate, palmitate, and stearate were digested with 60 c.c. of 50 per cent. alcohol for 2 hours at 60°, then cooled, and filtered. The fatty acids were liberated from the filtrate, washed, dried, and weighed, giving 0·270 grm. with a melting-point of 48·6° and a neutralisation value of 243. Since the yield was only about one-half of what it should be, the insoluble salts were again extracted with alcohol in the same manner,

yielding an insoluble residue weighing 0·928 grm. This time the acids were liberated from the insoluble residue and after being recrystallised from 60 per cent. alcohol showed a melting-point of 56·5° and a neutralisation value of 209·3. Calculated for a mixture of equal parts of stearic and palmitic acids: 56·4° and 208·3 respectively."

Palmitic Acid.—Palmitic acid is not easy to determine, in fact, no simple direct method has yet been suggested. It will remain with the stearic acid in the method of Jacobson and Holmes, and this mixture may then be separated by means of the method of Hehner and Mitchell described below under stearic acid, palmitic acid being determined by difference. Patel, Sudborough and Watson (*J.S.C.I.*, 1923, 42, 987A) have suggested that mixtures of stearic acid and palmitic acid may be examined by means of the melting-points of the methyl esters, of which they give tables. E. André (*ibid.*, 1922, 41, 639A) separates the acid from stearic acid by means of the fractional precipitation of the lithium salts from 95 per cent. alcohol.

Stearic Acid.—Some suggestions for the separation of palmitic and stearic acids are given under the former above. The usual method adopted for the determination of stearic acid is that due to Hehner and Mitchell (*Analyst*, 1896, 21, 321), which depends upon the fact that stearic acid is only slightly soluble in alcohol (S.G. 0·8183) at 0°. This process may be carried out in the following way :

Dissolve 3·5 grms. pure stearic acid in 500 c.c. of alcohol S.G. ·8183 (=94·4 per cent. by volume) in a stoppered bottle, and place in ice and water overnight. Next day, siphon off the supernatant alcohol by means of a thistle funnel, tied over the end with fine muslin, and connected with a vacuum-flask and filter-pump. Weigh into a squat wide-mouthed flask 1 grm. of solid (or 5 grms. if liquid) acid, and dissolve in 100 c.c. of above alcohol solution. Cool to 0° in ice overnight, and agitate to promote crystallisation. Filter off alcohol as before, keeping flask immersed in ice-water, using thistle funnel and vacuum-flask. Wash residue with three lots of 10 c.c. alcoholic stearic solution at 0°. Dissolve crystals adhering to muslin of thistle funnel with ether and add to flask, evaporate off, dry at 100° and weigh. Ascertain M.Pt. : should be not under 68·5° C.; if too low the treatment should be repeated. (In order to test if free from fatty acids of higher molecular weight, titrate with standard alkali.) Subtract from weight of crystals obtained ·005 grm. to allow for stearic acid due to alcoholic solution used. The balance of crystals is calculated to stearic acid per cent.

This process, on account of certain peculiarities which are probably due to supersaturation effects, but which have not yet been quite satisfactorily worked out, is apt to give capricious results unless the conditions are very carefully followed. Various workers have found that although certain fats give no precipitate in the test under ordinary conditions, yet when stearic acid is added to the fatty acids more is obtained on crystallisation than was put in. On this point reference should be made to the paper of Holland, Reed and Buckley (*Analyst*, 1916, 41, 209) and to a note by Mitchell (*Analyst*, 1924, 49, 515). Where this method is used, therefore, it is desirable to add about 0·1 gram of stearic acid and to subtract this from the final result. Mitchell suggests getting over the difficulty by shaking the flask vigorously after twelve hours and then allowing to stand a further 12 hours in the ice-water. The method appears to break down entirely in the case of japan-wax.

Arachidic and Lignoceric Acids.—These are determined together as described under arachis oil on page 260.

The Unsaturated Fatty Acids.—When these consist entirely of oleic acid its amount can, of course, be calculated directly from the iodine value

by simple proportion, whilst the presence of material quantities of more highly unsaturated acids will be indicated by a greater absorption of iodine than could be explained by 100 per cent. of oleic acid; where any amount of linolenic or more highly unsaturated acids are present they may be detected and approximately determined by means of the insoluble bromide value detailed on page 129. In the absence of such acids the proportion of oleic to linoleic acid in the liquid fatty acid may be determined to a certain extent simply from a determination of their iodine value. The further treatment of the bromine derivatives has already been explained on page 51.

CHAPTER VI

GLYCEROL

As has been already (page 12) explained at length glycerol, a trihydric alcohol, is an important constituent of oils and fats, from whence it is set free during saponification. Glycerol may also be prepared by fermentation processes (Connstein and Ludecke, *J.S.C.I.*, 1919, 38, 691A), but this latter process has not yet become a commercial proposition.

Chemically pure glycerol has a melting-point of 18°, whilst the boiling-point is 290° at 760 mm., 210° at 50 mm., 162° at 10 mm., and 143° at 0·2 mm. The S.G. at 15° is 1·2655. Such glycerol is, however, not easily obtainable on account of its hygroscopic nature. It is a colourless, transparent syrup liquid having a sweet burning taste, and miscible with water and with alcohol. It is insoluble in ether, chloroform or fixed oils.

Under normal conditions it is not usual to obtain glycerol in the crystalline condition, although slow crystallisation can be started by seeding with a crystal of the material when the bulk is well cooled. On one occasion, during a spell of cold winter weather, the author observed that a bottle labelled glycerol contained a considerable number of beautiful large crystals, which on examination proved to be glycerol only; this was a case of spontaneous crystallisation.

The B.P. contains the following requirements for the commercially pure substance: "Neutral to litmus. An aqueous solution (1 in 10) yields no characteristic reactions for ammonium, chlorides, or sulphates. Assumes, when heated, not more than a faint yellow but no pink colouration, and yields not more than a very slight charred residue and no odour of burnt sugar (absence of sugar). Undergoes no darkening in colour when mixed with an equal volume of solution of ammonia and a few drops of solution of silver nitrate, the mixture being kept protected from light and the observation being made after a lapse of five minutes (absence of formic acid, acrolein). Gently warmed with an equal volume of diluted sulphuric acid, the mixture being vigorously shaken, not more than a faint odour is noticeable (absence of fatty acids). Shaken with an equal volume of sulphuric acid, the mixture being kept cool, not more than a very slight straw colouration is produced (absence of extraneous organic matter). A mixture of 10 millilitres of glycerin with 40 millilitres of water, 1 drop of solution of ammonia, and 1 drop of solution of tannic acid, assumes not more than a faint and transient pink or purple colouration (limit of iron)."

Lead and copper should be absent, and there should not be a greater quantity of arsenic present than 4 parts per million. For oil examination it is particularly desirable that the glycerol used should be free from volatile fatty acids. Many samples of glycerol yield blank tests when treated by the Reichert-Polenske process of 2·0 and more. There is no necessity for such a blank to exceed 0·2 or 0·3, and other samples should be discarded.

The Determination of Glycerol

1. *Physical Methods.*—The strength of glycerol and water solutions, in the absence of other materials, may be adjudged either from the specific

gravity or from the refractive index. A table has been compiled by Lewkowitsch, giving the specific gravities of solutions of glycerol according to various observers, this table will be found in the Appendix on page 481. The coefficient of expansion of pure glycerol may be taken as practically 0·0006 for each degree centigrade, but will, of course, vary with the concentration. The following table, which gives the specific gravity of glycerol of various strengths and at various temperatures, has been compiled by E. Lewis (*J.S.C.I.*, 1922, 41, 97T).

TABLE XIV.—SPECIFIC GRAVITY OF GLYCEROL

% Gly.	15°/51°.	20°/20°.	25°/25°.	30°/30°.	35°/35°.	40°/40°.	45°/45°.	50°/50°.
5	1·0122	1·0117	1·0113	1·0108	1·0103	1·0098	1·0092	1·0087
10	1·0245	1·0237	1·0233	1·0227	1·0221	1·0215	1·0209	1·0203
15	1·0370	1·0358	1·0354	1·0350	1·0346	1·0340	1·0334	1·0328
20	1·0495	1·0489	1·0481	1·0474	1·0467	1·0460	1·0453	1·0446
25	1·0621	1·0610	1·0605	1·0600	1·0593	1·0586	1·0579	1·0572
30	1·0753	1·0747	1·0737	1·0729	1·0721	1·0713	1·0705	1·0697
35	1·0885	1·0880	1·0869	1·0861	1·0853	1·0845	1·0837	1·0829
40	1·1023	1·1017	1·0905	1·0896	1·0887	1·0878	1·0969	1·0960
45	1·1156	1·1150	1·1142	1·1134	1·1125	1·1116	1·1106	1·1095
50	1·1290	1·1283	1·1274	1·1263	1·1253	1·1240	1·1229	1·1220

This same observer (*loc. cit.*) has also compiled a table giving the composition of solutions of glycerol of varying specific gravities at 20°/20°, which is as follows:

TABLE XV.—PERCENTAGES OF GLYCEROL IN AQUEOUS SOLUTIONS

Sp. Gr. at 20°/20° C.	g. Gly. in 100 g.	c.c. Glyc. in 100 g.	g. Glyc. in 100 c.c.	c.c. Glyc. in 100 c.c.
1·0117	5·00	4·94	5·06	4·09
1·0237	10·00	9·76	10·24	8·10
1·0358	15·00	14·48	15·54	12·30
1·0489	20·00	19·06	20·98	16·60
1·0610	25·00	23·56	26·53	21·00
1·0747	30·00	27·91	32·24	25·52
1·0880	35·00	32·17	38·08	30·05
1·1017	40·00	36·31	44·07	34·89
1·1150	45·00	40·36	50·17	39·72
1·1283	50·00	44·31	56·41	44·56
1·1418	55·00	48·17	62·80	49·72
1·1550	60·00	51·95	69·30	54·86
1·1691	65·00	55·59	75·99	60·16
1·1827	70·00	59·18	82·79	65·54
1·1964	75·00	62·69	89·73	71·04
1·2091	80·00	66·16	96·73	78·58
1·2237	85·00	69·46	104·01	82·35
1·2368	90·00	72·77	111·31	88·13
1·2506	95·00	75·96	118·81	94·06
1·2631	100·00	79·17	126·31	100·00

The specific gravity of glycerol solutions has also been determined by Henkel and Roth (*Z. f. angew. Chem.*, 1905, 19, 1936); by Grün and Wirth (*J.S.C.I.*, 1919, 38, 295A); and by H. Wolff (*J.S.C.I.*, 1919, 38, 470A).

The refractive index is another valuable method of determination of the strength of glycerol solutions. The table given in the Appendix on page 480 gives the refractive index of glycerol solution according to the observations of Lenz, Strohmer and Skalweit respectively. The change in refractive index for 1° C. alters with the concentration; in the case of pure water it is 0·00008, whilst in the case of 95 per cent. glycerol it is 0·00032. Lenz has compiled a table which gives the difference between the refractive index of pure water and that for solutions of glycerol of various strengths, this table, which can be used by determining the figures for water and the glycerol solution in the same instrument and at the same temperature, is accurate at about 12·5°.

TABLE XVI.—REFRACTIVE INDEX OF GLYCEROL SOLUTIONS

Glycerol.	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol.	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol.	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.	Glycerol.	$n_{[D]}$ Glycerol $- n_{[D]}$ Water.
Per cent.		Per cent.		Per cent.		Per cent.	
100	0·1424	74	0·1046	48	0·0645	22	0·0288
99	0·1410	73	0·1032	47	0·0630	21	0·0275
98	0·1395	72	0·1018	46	0·0616	20	0·0261
97	0·1381	71	0·1003	45	0·0601	19	0·0238
96	0·1366	70	0·0987	44	0·0587	18	0·0225
95	0·1352	69	0·0970	43	0·0572	17	0·0212
94	0·1337	68	0·0952	42	0·0556	16	0·0199
93	0·1323	67	0·0933	41	0·0541	15	0·0186
92	0·1308	66	0·0915	40	0·0526	14	0·0173
91	0·1294	65	0·0897	39	0·0510	13	0·0160
90	0·1279	64	0·0889	38	0·0495	12	0·0146
89	0·1264	63	0·0861	37	0·0479	11	0·0133
88	0·1250	62	0·0842	36	0·0464	10	0·0120
87	0·1235	61	0·0824	35	0·0451	9	0·0108
86	0·1221	60	0·0806	34	0·0438	8	0·0096
85	0·1206	59	0·0792	33	0·0424	7	0·0083
84	0·1191	58	0·0780	32	0·0411	6	0·0071
83	0·1177	57	0·0768	31	0·0398	5	0·0058
82	0·1162	56	0·0757	30	0·0385	4	0·0046
81	0·1148	55	0·0745	29	0·0372	3	0·0033
80	0·1133	54	0·0731	28	0·0358	2	0·0021
79	0·1119	53	0·0717	27	0·0345	1	0·0008
78	0·1104	52	0·0702	26	0·0332	0	0·0000
77	0·1090	51	0·0688	25	0·0318		
76	0·1075	50	0·0663	24	0·0315		
75	0·1061	49	0·0659	23	0·0302		

The refraction of glycerol solutions has also been determined by Grün and Wirth (*J.S.C.I.*, 1919, 38, 295A), and by H. Wolff (*J.S.C.I.*, 1919, 38, 470A).

Grün and Wirth (*loc. cit.*) consider that the boiling-point method is the

most accurate way of determining the concentration of aqueous solutions of glycerol. They have determined the boiling-point of solutions of various strengths. This work has been repeated by E. Lewis (*J.S.C.I.*, 1922, 41, 97T) whose results, given in the table below, agree closely with those of the earlier workers.

TABLE XVII.—BOILING-POINTS OF AQUEOUS SOLUTIONS OF GLYCEROL AT 760 MM. PRESSURE (LEWIS)

% Glycerol.	°C.	% Glycerol.	°C.	% Glycerol.	°C.
100	290·0	90	137·5	40	104·2
99	225·5	85	126·8	35	103·5
98	196·0	80	121·5	30	103·0
97	179·5	75	116·5	25	102·4
96	168·0	70	113·5	20	102·0
95	160·0	65	111·0	15	101·5
94	156·0	60	108·8	10	101·0
93	149·5	55	107·2	5	100·5
92	145·5	50	106·0		
91	141·0	45	105·5		

The boiling-point of glycerol solutions has also been studied by Von Mayer-Bugström (*J.S.C.I.*, 1924, 43, B877).

I. M. Kolthoff (*J.S.C.I.*, 1918, 37, 250A) has suggested a method for the determination of water in glycerol by means of the observation of the temperatures of miscibility with pure aniline under standard conditions.

2. *Chemical Methods.—Hehner's bichromate Method.*—This method depends upon the oxidation of glycerol with a solution of potassium dichromate, the following procedure is that adopted by the International Committee on Glycerin Analysis.

Reagents required:

(*a*) Pure Potassium Bichromate powdered and dried in air free from dust or organic vapours, at 110° to 120° C. This is taken as the standard.

(*b*) Dilute Bichromate solution—7·4564 grms. of the above bichromate (*a*) are dissolved in distilled water, and the solution made to 1 litre at 15·5° C.

(*c*) Ferrous Ammonium Sulphate.—Dissolve 3·7282 grms. of potassium bichromate (*a*) in 50 c.c. of water. Add 50 c.c. of 50 per cent. (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing-bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (*b*). Calculate the value of the ferrous salt in terms of bichromate.

(*d*) Silver Carbonate.—This is prepared as required for each test from 140 c.c. of 0·5 per cent. silver sulphate solution by precipitation with about 4·9 c.c. N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant, and wash once by decantation.

(*e*) Subacetate of Lead.—Boil a pure 10 per cent. lead acetate solution with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(*f*) Potassium Ferricyanide.—A very dilute solution containing about 0·1 per cent.

The Method.—Weigh 20 grms. of the glycerol, dilute to 250 c.c., and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about ten minutes, and add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (*e*), allow to stand a few minutes, dilute with distilled water to 100 c.c., and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c. and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c.c. is ample.) Occasionally a crude glycerol will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerol should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 grms. of the powdered potassium bichromate (*a*). Rinse down the bichromate with 25 c.c. of water, and stand with occasional shaking until all the bichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours, and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing-bottle a slight excess of the ferrous ammonium sulphate (*c*), making spot tests on a porcelain plate with the potassium ferricyanide. Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 grm. glycerol = 7·4564 grms. bichromate
1 grm. bichromate = 0·13411 grm. glycerol.

Notes.—1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

2. Before the bichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

3. For " crudes " practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0·5 c.c.

4. It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

The dichromate method is considered by Tortelli and Ceccherelli (*Analyst*, 1914, 39, 181) to give excellent results when carried out according to their modifications (q.v.), but Hehner (*loc. cit.*) rightly points out that it is necessary to determine and subtract the dichromate value of any non-volatile impurity. Nearly all organic impurities will effect this method and yield high results. Normann and Hugel (*J.S.C.I.*, 1916, 35, 932) speak well of it.

Modifications of the method have been suggested by Richardson and Jaffé (*J.S.C.I.*, 1898, 17, 330), Little and Fenner (*J.S.C.I.*, 1917, 36, 893), and H. B. Bennett (*J.S.C.I.*, 1924, 43, B1019). Some workers have also made use of the quantity of carbon dioxide produced during the reaction. Cf. Fachini and Somazzi (*Analyst*, 1924, 49, 245).

The Permanganate Method.—This method depends upon the fact that

when glycerol is oxidised by a strongly alkaline solution of potassium permanganate it is entirely converted into oxalic acid.

$$C_3H_8O_3 + 3O_2 = C_2H_2O_2 + CO_2 + 3H_2O$$

The method was first suggested by Wanklyn and Fox and was later worked out by Benedikt and Zsigmondy (*J.S.C.I.*, 1885, 4, 610). For the determination weigh out an amount of the sample equivalent to about 0·2 to 0·3 gram of glycerol and dilute to about 250 c.c. with water in a large flask. Add about 10 grams of solid potassium hydroxide and then either finely-powdered solid potassium permanganate or a 5 per cent. solution until the liquid ceases to be green and becomes either blue or black. Boil the solution which will cause the separation of hydrates of manganese dioxide and then discharge the red colouration of the solution by the addition of sulphurous acid; excess of sulphite must be avoided. Filter and wash the filter-paper with hot water ignoring any turbidity in the wash filtrates. Acidify the filtrate with acetic acid, heat to the boiling-point and precipitate with 10 c.c. of a 10 per cent. solution of calcium chloride. After standing for some time the precipitated calcium oxalate is filtered off, washed with hot water, and titrated with N/10 permanganate in the usual way.

1 c.c. N/10 $KMnO_4$ = 0·0046 gram glycerol

The method has been modified by Herbig by the use of hydrogen peroxide in place of sulphurous acid on account of the possible errors caused by the latter. This method is recommended by Mangold (*J.S.C.I.*, 1891, 10, 803), who shows that the difficulties encountered by Johnstone (*J.S.C.I.*, 1891, 10, 204) were caused by lack of attention to the details of the method; the same conclusion was reached by Hehner (*J.S.C.I.*, 1891, 10, 204).

The Acetin Method.—This method depends upon the fact that when glycerol is heated with acetic anhydride it is converted quantitatively into triacetin. The following details for carrying out the process are those suggested by the International Committee.

The following reagents are required :

1. Best Acetic Anhydride.—This should be carefully selected. A good sample must not require more than 0·1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7·5 c.c., only a slight colour should develop during digestion of the blank.

2. Pure Fused Sodium Acetate.—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

3. A Solution of Sodium Hydroxide for Neutralising, of about N/1 strength, free from carbonate.—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through an asbestos or paper-filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

4. N/1 Sodium Hydroxide, free from carbonate.—Prepared as above and carefully standardised.

Some sodium hydroxide solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

5. N/1 Acid.—Carefully standardised.

6. Phenolphthalein solution.—0·5 per cent. phenolphthalein in alcohol and neutralise.

The Method.—Into a narrow-mouthed flask (preferably round-bottomed) capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 grms. of the glycerol. Add first about 3 grms. of the anhydrous sodium acetate, then 7·5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground-glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon-dioxide-free distilled water, heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding the water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper of ground-glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (6), then run in sodium hydroxide solution (3) or (4) until a faint pinkish-yellow colour appears throughout the solution. This neutralisation must be done most carefully. The alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of N/1 NaOH (4), and note carefully the exact amount. Boil gently for fifteen minutes, the flask being fitted with a glass tube acting as a partial condenser; cool as quickly as possible, and titrate excess of NaOH with N/1 acid (5) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

From the N/1 NaOH consumes calculate the percentage of glycerol after making the correction for the blank test described below :

1 c.c. of N/1 NaOH = 0·03069 grm. of glycerol

The coefficient of expansion for normal solutions is approximately 0·00033 per c.c. for each degree C. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using

the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid, it is not necessary to add more than 5 c.c. of the N/1 alkali (4), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

Determination of the Glycerol Value of the Acetylisable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 c.c. of water, washed into a clean acetylising flask 120 c.c. capacity, and the water evaporated. Now add anhydrous sodium acetate, and proceed as in the glycerol determination before described. Calculate the result to glycerol.

Analysis of Acetic Anhydride.—Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenolphthalein and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing-bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample, stopper, mix, allow to cool, and weigh. Wash contents into about 200 c.c. cold water, and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 grms.) and double result, obtaining c.c. N/1 NaOH per 100 grms. sample. One c.c. NaOH equals 0·0510 grm. of acetic anhydride.

Other Methods.—S. H. Bertram (*J.S.C.I.*, 1915, 34, 288) has suggested the use of an alkaline copper sulphate solution with subsequent addition of potassium iodide and liberation of the iodine produced by means of sodium thiosulphate.

H. Bull (*Analyst*, 1916, 41, 343) has suggested the use of sodium glyceroxide and reports that he obtains useful results.

Strebinger and Streit (*J.S.C.I.*, 1924, 43, B640) have proposed the use of potassium iodate in concentrated sulphuric acid solution, the excess of iodate being determined by the addition of potassium iodide and titration of the liberated iodine.

Ziesel and Fanto determine glycerol by converting it into isopropyl iodide. The glycerol is treated with hydriodic acid in the presence of red phosphorus, which converts it into isopropyliodide. This is distilled into silver nitrate solution which causes the quantitative precipitation of silver iodide. This method has been shown by Lewkowitsch (*Analyst*, 1903, 28, 108) to give low results although a modified method of Willstatter and Madinaveitia (*Analyst*, 1912, 37, 571) has been reported by them to give results nearer the truth. This has been confirmed by Normann and Hugel (*J.S.C.I.*, 1916, 35, 932).

Method Recommended.—Practically the whole of the above-described methods will give identical results in the case of solutions of pure glycerol; the physical methods will be preferred as requiring less manipulation. The refraction method takes the least time and will, therefore, be used for routine work.

In the presence of impurities all of the oxidation methods will give high results, and in this case the acetin process will give accurate results when the acetyl value of the non-volatile products is taken into account as described above. The method of determining glycerol in oils and fats is described in the following paragraph:

Determination of Glycerol in Fats.—A suitable quantity of the fat is

saponified with alcoholic potash in the usual way (where the permanganate process is used, the alcohol should be methyl alcohol as ethyl alcohol may produce small quantities of oxalic acid under the conditions of the experiment). Most of the alcohol is evaporated at a lower temperature (to guard against loss of glycerol by volatilisation which is considerable at temperatures above 70°), the soap is dissolved in water and the fatty acids liberated by the addition of a slight excess of hydrochloric acid. The liquid is allowed to cool by standing, when the fatty acids may be filtered off and washed. The filtrate, which contains the glycerol, may then be treated as a very dilute crude glycerin. For the acetin process it should be neutralised with excess of barium carbonate, and evaporated to small bulk on the water-bath. The residue extracted with a mixture of ether and alcohol, the extracts being mixed and evaporated at a low temperature.

K. Fleischer (*J.S.C.I.*, 1921, 40, 865A) suggests that the glycerin be distilled off under reduced pressure, and the amount determined from the specific gravity of the distillate, as in the case of alcohol.

Hoyt and Pemberton (*J.S.C.I.*, 1922, 41, 260A) determine glycerol in the presence of sucrose by the determination of the total dichromate value of the solution, and subtracting that due to the sucrose the amount of which is determined separately by the usual methods.

Glycerol solutions may be purified to a large extent by the addition of basic lead acetate, and then removal of the excess of lead with hydrogen sulphide in the usual manner. In this way the interference with the chemical method of determination will be much reduced (cf. K. Fricke, *J.S.C.I.*, 1922, 41, 148A).

The Examination of Glycerin.—Commercial glycerins should be examined by the methods of the International Committee. These are given below:

Sampling.—The most satisfactory method available for sampling crude glycerol liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerol. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerol to be taken, including any deposit.

Analysis.—1. *Determination of Free Caustic Alkali.*—Weigh 20 grms. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly-boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid (N/1). Calculate to percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grms. of the sample in a platinum dish, burn off the glycerol over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash,

and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. *Determination of Alkali present as Carbonate.*—Take 10 grms. of the sample, dilute with 50 c.c. distilled water, add sufficient N/1 acid to neutralise the total alkali found at (2), boil under a reflux condenser for fifteen to twenty minutes, wash down the condenser tube with distilled water, free from carbon dioxide and titrate back with N/1 NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. *Alkali combined with Organic Acids.*—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.*—Take 10 grms. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with N/1 NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 grms.

6. *Determination of Total Residue at* 160° C.—For this determination the crude glycerol should be slightly alkaline with Na_2CO_3, not exceeding the equivalent of 0·2 per cent. Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerols, this alkalinity must not be exceeded.

Preparation of Glycerol.—Ten grms. of the sample are weighed into a 100 c.c. flask, diluted with water, and the calculated quantity of N/1 HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petrie or similar dish 2·5 inches diameter and 0·5 inch deep, which should have a flat bottom. In the case of crude glycerols abnormally high in organic residue, a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mgrms.

Evaporation of the Glycerol.—The dish is placed on a water-bath (the top of the 150° C. oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 inches cube, having an iron plate $\frac{3}{4}$ inch thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerol is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° C. can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

An addition of 0·5 to 1 c.c. of water is made, and by a rotatory motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two or three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is than subjected to a second baking of one hour, after which the dish

is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1·5 mgrms. per hour is obtained.

Corrections to be applied to the Weight of the Total Residue.—In the case of acid glycerol, a correction must be made for the alkali added. 1 c.c. of N/1 alkali represents an addition of 0·022 grm. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight, multiplied by 100, gives the percentage of total residue at 160° C.

Preserve the total residue for the determination of the non-volatile acetylisable impurities.

7. *Organic Residue.*—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO_3 radicle thus derived is not included in the organic residue.)

8. *Moisture.*—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride.

2 or 3 grms. of very pure bulky asbestos freed from acid-soluble material, which has been previously dried in a water-oven, are placed in a small stoppered weighing-bottle of about 15 c.c. capacity. The weighing-bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 5 grms. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about forty-eight hours. At low temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

Dichromate Process for Glycerol Determination.—See above page 66.

Instructions for Calculating Actual Glycerol Content.—1. Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities, if any be present.

2. Determine the total residue at 160° C.

3. Determine the acetin value of the residue at (2) in terms of glycerol.

4. Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

Notes and Recommendations.—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160° C. and corrected acetin result, comes to within 0·5 of 100. Further, in such "crudes" the dichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities, such as polyglycerols or trimethylene glycol, are present. Trimethylene glycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and dichromate results of such distillates, trimethylene glycol showing by the former method 80·69 per cent., and by the latter 138·3 per cent., expressed as glycerol.

In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates.

The methods for detecting and determining these impurities have not formed the subject of this investigation.

Recommendations by Executive Committee.—If the non-volatile organic residue at 160° C. in the case of a soap lye " crude " be over 2·5 per cent.—i.e., when not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method, and any excess of glycerol found over 0·5 per cent. shall be deducted from the acetin figure.

In the case of saponification, distillation, and similar glycerol, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent., the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 per cent.) shall be deducted from the percentage of glycerol found by the acetin test.

BRITISH STANDARD SPECIFICATIONS FOR CRUDE GLYCERINS

The following standard specifications were drawn up by the British Executive Committee on crude glycerin analysis, and approved at a general meeting of crude glycerin-makers, buyers, and brokers, held in London on 3rd October 1912 :

Soap Lyes, Crude Glycerin.—Analyses to be made in accordance with the International Standard Methods (*supra*).

Glycerol.—The standard shall be 80 per cent. of glycerol. Any crude glycerin which tests 81 per cent. of glycerol or over shall be paid at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerin which tests under 80 per cent. of glycerol, but is 78 per cent. or over, shall be subject to a reduction of 1½ times the shortage, calculated at a *pro rata* price as from 80 per cent. If the test falls below 78 per cent. the buyer shall have the right of rejection.

Ash.—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent., but not exceeding 10·5 per cent., a percentage of deduction shall be made for the excess calculated as from 10 per cent. at *pro rata* price, and if the percentage of ash exceeds 10·5 per cent., but does not exceed 11 per cent., an additional percentage deduction shall be made to double the amount in excess of 10·5 per cent. If the amount of ash exceeds 11 per cent. the buyer shall have the right of rejection.

Organic Residue.—The standard shall be 3 per cent. A percentage deduction shall be made of 3 times the amount in excess of the standard of 3 per cent. calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3·75 per cent.

Saponification Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 88 per cent. Any crude glycerin tendered which tests 89 per cent. or over shall be paid for at a *pro rata* increase calculated as from the standard of 88 per cent. Any crude glycerin which tests under 88 per cent., but is 86 per cent. or over, shall be subject to a reduction of 1½ times the shortage calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent. the buyer shall have the right of rejection.

Ash.—The standard shall be 0·5 per cent. In the event of the ash exceeding 0·5 per cent., but not exceeding 2·0 per cent., a percentage reduction shall be made equal to double the amount in excess of 0·5 per cent. If

the amount of ash exceeds 2·0 per cent. the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent. calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

Other papers likely to be of interest in connection with the evaluation of glycerins and which may be consulted are here given:

" The Examination of Whale Oil Glycerin." A. H. Salway, *J.S.C.I.*, 1918, 37, 123T.

" The Purification of Commercial Glycerins." P. Bertolo, *J.S.C.I.*, 1919, 38, 832A.

" The Determination of Trimethylene Glycol in Glycerin." C. A. Rojahn, *J.S.C.I.*, 1920, 39, 314A.

" The Manufacture of Glycerol." Verbeek, *J.S.C.I.*, 1920, 39, 790A.

" The Determination of Trimethylene Glycol in Crude Glycerin." Cocks and Salway, *J.S.C.I.*, 1922, 41, 17T, 32T.

" Substitutes for Glycerol." Neuberg and Reinfurth, *J.S.C.I.*, 1920, 39, 801A.

" The Purification of Glycerin from Volatile Fatty Acids and their Esters." Kailan and Obogi, *J.S.C.I.*, 1925, 44, B325.

CHAPTER VII

QUALITATIVE TESTS

The Elaidin Test

The elaidin test depends upon the solid body which nitrous acid produces when acting upon oleic glycerides (a note on the cause of the reaction has been contributed by S. Fokin, *J.S.C.I.*, 1911, 30, 36). It has been used chiefly in the examination of olive oil and under some conditions will show 5 per cent. of adulteration, but as most adulterants are shown with equal ease by other methods it is now seldom used.

Various of the older methods have been tested by Archbutt (*J.S.C.I.*, 1886, 5, 304), who has come to the conclusion that the test must not be made below 25° and that the length of time required for solidification is of much more importance than the degree of solidity obtained. He applies the test in the following way :

18 grms. of mercury are placed in a dry stoppered 50 c.c. cylinder, and 15·6 c.c. of nitric acid, specific gravity 1·42, are added from a burette. The nitrous acid is entirely absorbed with production of a green colouration; as long as the reagent retains its green colour, it is fit for use. 8 grms. of the reagent are shaken up with 96 grms. of the oil in a wide-mouthed stoppered bottle, placed in water at the required temperature, and again shaken at intervals of ten minutes during two hours.

The results obtained by carrying out this test with different oils may be placed in four classes :

1. A solid hard mass. Olive, almond, arachis, lard, etc.
2. A buttery mass. Neat's-foot oil, Arctic sperm, etc.
3. Fluid with solid flocks. Sunflower oil, cotton-seed oil, sesamé oil, rape oil, etc.
4. Liquid. Linseed oils and drying oils.

At 25° olive oil takes from 200 to 400 minutes to solidify, whilst adulterated oils usually take longer than this, whilst the final product is not so hard.

The Sulphur Chloride Test

T. B. Warren (*Chemical News*, 1888, 57, 113), basing his results on the work of several previous investigators investigated the action of sulphur chloride on various oils in which cases gelatinous rubber-like masses are produced, which are more or less insoluble in carbon bisulphide according to the type of oil used. The method, which consists in adding a mixture of 2 c.c. of sulphur chloride and 2 c.c. of carbon bisulphide to 5 grams of the oil in a large crucible and warming, has been examined by C. O. Weber (*J.S.C.I.*, 1894, 13, 11) and Lewkowitsch, but has not been widely used. For further information the reader is, therefore, referred to these sources.

Colour Reactions

In general, colour reactions are produced not by the glycerides themselves but by impurities of various kinds which are extracted along with the oils from their sources. It follows, therefore, that as modern methods tend more and more to remove impurities, that oils will become more and more unlikely to respond to tests which depend upon such impurities.

Many workers have proposed a series of colour reactions with various reagents in order that fats might be distinguished one from another, but all these have long since been given up. A few colour reactions which, being recognised as valuable, are still used, such as the Halphen reaction, are described in some detail below. A few of the more recent suggestions are mentioned here, but in general even the better tests must be used with caution, whilst by far the larger proportion is worse than useless.

The Bellier-Kreis Reaction.—This is produced by shaking 5 c.c. of the liquid fat with 5 c.c. of nitric acid (S.G. 1·4) and 5 c.c. of a cold saturated solution of resorcinol in benzene (Bellier) or 5 c.c. of a 0·1 per cent. ethereal solution of phloroglucinol (Kreis). Seed oils give a colouration varying from pink through violet to brown, whilst animal fats give no immediate colouration. This only refers to normal oils prepared under certain conditions; there are many exceptions.

The Welmans Phosphomolybdic Acid Test.—This test is carried out (*J.S.C.I.*, 1892, 11, 548) by shaking 2 c.c. of a freshly-prepared solution of phosphomolybdic acid with 1 gram of the fat dissolved in 5 c.c. of chloroform. According to Welman the upper layer formed on standing develops a green colour in the case of cod-liver oil and vegetable oils, which is changed to blue on the addition of alkali; but no such changes are obvious in the case of animal fats other than cod-liver oil.

This test has been examined by Kühn and Halfpaap (*Analyst*, 1906, 31, 413), who attach very little value to it, by Lewkowitsch, who considers that at the best it may only be regarded as a preliminary test, and by Seiger, who modifies the reagent by the use of 0·1 gram of sodium molybdate in 10 c.c. of concentrated sulphuric acid, but who reports unsatisfactory results.

The Sulphuric Acid Liver Oil Test

This test, which was at one time considered to be diagnostic for fish liver oils, but which is now recognised as having a more general application, is described by the Pharmacopœia of the U.S.A. as follows:

" A solution of 1 drop of the oil in 1 mil. of chloroform, when shaken with one drop of sulphuric acid, acquires a violet-red tint, gradually changing to reddish brown."

It has received attention recently by Drummond and Watson (*Analyst*, 1922, 47, 341), and Harden and Robison (*Analyst*, 1923, 48, 226), who have endeavoured to isolate the substance producing the reaction, and by Richmond and England (*Analyst*, 1922, 47, 431), and Evers and Foster (*Analyst*, 1923, 48, 58) who have improved the technique of the process. The reaction is given also by butter fat, N. Sjörslev (*Analyst*, 1925, 50, 145).

Evers and Foster carry out the test in the following way: The required amount of oil, or of a solution of the oil in petroleum spirit, is measured into a test-tube; two drops of olive oil or some other natural oil, which itself gives no suspicion of colour with the test in any quantity, are added, and then petroleum spirit to 3 c.c. Seven c.c. of petroleum spirit are shaken violently in a small stoppered cylinder with one drop of sulphuric acid until the acid is completely broken up into small drops. The mixture is then quickly

poured into the test-tube. The drops of acid rapidly sink to the bottom, the violet colour forming in the petroleum spirit as they sink. In this way the colour is uniformly distributed throughout the solution, and the results are more consistent. Care must be taken that only small drops of sulphuric acid fall into the test-tube.

Carrying out the test as above (with addition of olive oil) they obtained the following results with various samples of oil:

TABLE XVIII.—RESULTS OF SULPHURIC ACID LIVER OIL TEST (EVERS AND FOSTER)

Oil.	Minimum Quantity giving Colour. c.c.	Colour.
Cod-liver oil (cattle)	0·01	blue-violet
Cod-liver oil (Newfoundland) unrefined .	0·015	,,
Cod-liver oil (North Sea A)	0·015	,,
Cod-liver oil (North Sea B)	0·015	,,
Cod-liver oil (refined) unknown origin .	0·015	,,
Whale oil	0·015	red-violet
Ling-liver oil	0·02	blue-violet
Cod-liver oil (North Sea C)	0·03	,,
Cod-liver oil, Norwegian unrefined . .	0·035	,,
Cod-liver oil, Norwegian refined . . .	0·035	,,
Mixed liver oil, unknown origin . . .	0·07	,,
Cod-liver " Stearin "	0·08	red-violet
Butter (three samples, A, B and C) . .	0·02	,,
Butter D	0·02	brown

These authors point out that it is necessary to treat the petroleum spirit (B.Pt. 40°–60°) by thoroughly shaking with sulphuric acid and separating, before it is used as the oil solvent, as otherwise the test may lose its sensitiveness.

The cause of the reaction is still uncertain. Drummond and Watson (*loc. cit.*) have shown that the substance responsible is contained in the livers of many species as far removed as man, frog and dog fish. It appears to be a normal constituent of the liver, and is not derived from the bile. The chemical nature of the substance has not been ascertained. It forms a low proportion of the unsaponifiable fraction, is not cholesterol, and probably not a member of the lipochrome pigments. It is thermo-stable in the absence of air or oxygen, but is rapidly destroyed by oxidation. The few properties of the substance which are known, as well as the available data regarding its distribution in natural products, show certain resemblances to the unidentified dietary unit known as vitamin A; and without assuming the identity of the two factors, it is suggested that the association may be of some significance. The colour test cannot be regarded as specific for liver fats, although they usually give the most intense reactions. The body fat, and fat from other organs of animals, especially if they have been fed on liver oils, may give the reaction.

Harden and Robinson (*loc. cit.*) have shown that a purple colour resembling that given by this reaction may be obtained by the addition of sulphuric acid to a petroleum spirit, or chloroform solution of cholesterol containing furfuraldehyde or *w*-hydroxy-methylfurfuraldehyde. Also, the addition of furfuraldehyde to oils yielding only a faint colouration gives rise

to an intense purple colour on the addition of sulphuric acid. Attempts were made to obtain furfuraldehyde or a substance capable of replacing it in this reaction from coal fish oil, but without success. The reaction is a delicate test for cholesterol, a faint purple colour being produced by 0·1 mgrm. in 5 c.c. of petroleum spirit.

So Uchida (*J.S.C.I.*, 1916, 35, 1091) has stated that akebi-seed oil assumes with one drop of sulphuric acid a greenish-yellow colour, which becomes a cochineal-red colour on stirring.

The Liebermann-Storch Test

This test which is valuable for the detection of rosin oil may be carried out as follows:

Gently warm a small quantity of the sample with an equal volume of pure acetic anhydride: cool.

Pipette off the acetic anhydride layer, and add to it one drop of sulphuric acid, S.G. 1·53 (by mixing equal quantities concentrated sulphuric acid and water).

In presence of rosin a violet colouration (rapidly fugitive) is produced.

This reaction is given by cholesterol. This will not be very serious in the case of a linseed oil which should contain no cholesterol, but as a safe method of confirmation the oil may be saponified with alcoholic potash, the mixture acidified and the test applied to the liberated fatty acids.

The Halphen Reaction

Certain colour reactions of cotton-seed oil were first noticed by Halphen in 1894 (*Analyst*, 1894, 19, 282), whilst three years late the same worker published his method in more or less its present form (*Analyst*, 1897, 22, 326). The test may be carried out as follows:

" Mix carbon disulphide, containing about 1 per cent. of sulphur, in solution, with an equal volume of amyl alcohol. Mix equal volumes of this reagent and the oil under examination, and heat in an oil-bath at 120° for 1 hour. In the presence of as little as 1 per cent. of cotton-seed oil, a characteristic red or orange-red colour is produced.

" Lard and lard oil from animals fed on cotton-seed meal will give a faint reaction; their fatty acids also give this reaction.

" The depth of colour is proportional, to a certain extent to the amount of oil present, and by making comparative tests with cotton-seed oil some idea as to amount present can be obtained. Different oils react with different intensities, and oils which have been heated from 200°–210° react with greatly diminished intensity. Heating 10 minutes at 250° renders cotton-seed oil incapable of giving the reaction."

Since the reaction was first suggested for cotton-seed oil it has been discovered that various other oils also give the reaction. Thus, in 1913, Sprinkmeyer and Diedrichs (*Analyst*, 1913, 38, 467) showed that the reaction was given to a greater extent by kopak oil (q.v.), Bolton and Jesson (*Analyst*, 1915, 40, 7) have shown that calumpang-seed oil gives the reaction as strongly as does cotton-seed oil, whilst Jamieson and Baughman (*J.S.C.I.*, 1920, 39, 417A) found that the oil of okra seed (*Abelmoschus esculentus*) also gives the reaction to a certain extent.

All samples of cotton-seed oil do not give the reaction to the same extent, but in the case of any one sample of oil the depth of colour obtained in the reaction is proportionate to the amount of the cotton-seed oil present

in mixtures. The substance present in cotton-seed oil which causes the colouration is destroyed by heating the oil to about 250° so that oils so treated no longer answer to this test, whilst treatment of the oil with sulphurous acid or chlorine has the same effect.

It has been shown by various workers that the fat of animals fed on cotton-seed cake frequently gives a positive reaction with the test, so that even a positive reaction must not be taken as final evidence of actual adulteration unless the quantity indicated approaches 10 per cent (cf. pages 369 and 400).

A number of suggestions have been made with the object of making the test more sensitive. As has been pointed out by Bolton and Revis (*Analyst*, 1915, 40, 500), this is of some importance, on account of the diminution in the degree of the reaction by hydrogenation and other methods of treatment to which oils are now subjected.

Rupp (*Analyst*, 1907, 32, 95) suggested performing the test in closed tubes, using a water-bath and heating for 45 minutes, which method is considered by Wagner and Clement (*Analyst*, 1908, 33, 396) to be advantageous. Marcille (*Analyst*, 1910, 35, 356) uses closed tubes, and heats to 120°, and states that 1 per cent. of cotton-seed oil shows up well under these conditions. F. F. Shelley (*Analyst*, 1925, 50, 132) also supplied the closed-tube method. Garnier (*Analyst*, 1909, 34, 229) heats with excess of undissolved sulphur under a reflux condenser, but this would not appear to have any particular advantage over the ordinary method.

Rosenthaler (*Analyst*, 1910, 35, 536) found that it is not necessary to use amyl alcohol, but that methyl, ethyl, propyl and isobutyl alcohols also give the reactions as do also benzyl, allyl alcohols, etc. He found, however, that it was not possible to replace the sulphur by other sulphur compounds such as mustard oil, etc.

Gastaldi (*J.S.C.I.*, 1912, 31, 934) states that it is to the impurities contained in the amyl alcohol that the reaction must be ascribed, and this worker found that pyridine, aniline and other substances, including ammonia and caustic soda give the reaction, some of them to a greater degree than does amyl alcohol. He carries out the test by mixing together 5 c.c. of the oil, 1 drop of pyridine and 4 c.c. of carbon bisulphide containing 1 per cent. of sulphur, and heating the mixture in a water-bath for half an hour. As little as 0·25 per cent. of cotton-seed oil may be detected in this way.

Utz (*Analyst*, 1914, 39, 92) mixes the oil with an equal volume of a 1 per cent. solution of sulphur in pentachlorethylene, and heats to boiling. Gastaldi (*J.S.C.I.*, 1914, 33, 1214) has examined this test and finds that it is uncertain and not characteristic, whilst he has modified his own test (*vide supra*) by using a smaller quantity of carbon bisulphide, a larger quantity of pyridine and heating for 5 minutes at a temperature not above 140°.

The Process Recommended.—Place 5 c.c. of the oil in a test-tube and add thereto 4 c.c. of carbon bisulphide containing 1 per cent. of sulphur and 4 c.c. of amyl alcohol, and heat the mixture in an oil-bath at 130° for half an hour—by this means the merest traces of cotton-seed oil may be detected, providing that the oil used is capable of giving a positive reaction.

The Becchi Reaction

The fact that cotton-seed oil exerts a reducing action on an alcoholic solution of silver nitrate was first used as a method of identification by Becchi (*Analyst*, 1887, 12, 170). The test as described by Becchi may be carried out as follows :

The reagent is prepared by dissolving 1 gram of silver nitrate in a mixture of 98·5 c.c. of alcohol (absolute), 20 c.c. of ether and 1·5 c.c. of N/2 nitric acid. 5 grams of the oil are heated with 2·5 c.c. of the reagent in boiling water for ten minutes when in the presence of cotton-seed oil a darkening of the solution will take place. A committee appointed by the Italian Government recommended that amyl alcohol and colza oil be added to the Becchi reagent, but no good purpose would seem to be served by this complication.

The Becchi reaction suffers all the shortcomings of the Halphen reaction, e.g., it is not given by heated oils or old oils, whilst oils from different sources give the reaction to different degrees, and in addition one or two which are peculiar to itself. The test may be used occasionally as a corroborative one, but it is doubtful whether the results obtained ever repay the trouble involved.

Milliau (*J.S.C.I.*, 1893, 12, 716) modified the test by working on the fatty acids in place of the oil itself and proceeds as follows :

5 c.c. of the fatty acids of the sample are dissolved in 15 c.c. of 95 per cent. alcohol, and heated in a water-bath to 90°. 2 c.c. of a 30 per cent. solution of silver nitrate are then added, and the mixture is again heated until about one-third of the alcohol has evaporated. If the sample be cotton-seed oil, or contain cotton-seed oil, the silver nitrate is reduced to metallic silver, producing a black or brown colour in the liquid, or giving particles of reduced silver.

Wiley has reported favourably on this test, but neither Hehner nor Lewkowitsch consider it to be any improvement, the latter indeed reporting that it is less useful and that in some cases a positive result may be obtained by the original test and a negative one by Milliau's modification. This fact was later explained by Muntz, Durand and Milliau, who showed that the reducing substance is soluble in water and was removed from the fatty acids by repeatedly washing with water. Milliau has, therefore, modified the test in the following manner :

15 c.c. of the oil are saponified in a 250 c.c. porcelain dish with alcoholic potash, and the soap is dissolved in 150 c.c. of distilled water. The alcohol is evaporated off by boiling, and the fatty acids are liberated by adding a slight excess of dilute sulphuric acid. The solution must not be boiled in order to melt the separated fatty acids, as otherwise the aldehydic substances may pass into the aqueous solution. The emulsified acids are taken off and washed in a wide test-tube three times each with 10 c.c. of cold distilled water. Finally, the fatty acids are dissolved in 15 c.c. of 92 per cent. alcohol and 2 c.c. of a 3 per cent. silver nitrate solution are added. The test-tube is placed, protected from light, in a water-bath and heated to 90° until one-third of the alcohol has evaporated off. 10 c.c. of hot distilled water are then added, and the heating continued for a few minutes. In the presence of cotton-seed oil, the fatty acids which float on the top are black, owing to the separation of metallic silver. If the proportion of cotton-seed oil exceeds 15 per cent. the aqueous solution is also coloured.

As a modification of this method Jean adds petroleum ether to the soap, so that on liberating the fatty acids they will be dissolved when the petroleum ether solution may be washed with water without loss of the reducing substance and tested with the reagent in the usual way.

A further modification of the Milliau method has been suggested by Tortelli and Ruggeri, who proceed as follows :

5 grms. of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 per cent. silver nitrate solution is added; the sample is then heated on a water-bath to 70°–80°. They state that cotton-

seed oil reduces the silver immediately, whereas olive oil and other oils remain clear for some time, and that even cotton-seed oil, which had been heated to 250° for ten and twenty minutes respectively, could be recognised when present in as low a proportion as 10 per cent. in olive oil, on allowing the liquid fatty acids of the mixed oil to stand in the hot water-bath for several hours.

Petkow (*Analyst*, 1907, 32, 123) has stated that the substances causing the Halphen and Becchi reactions are not identical, so that there may be, after all, some point in applying both tests in doubtful cases. Petkow states that care must be taken in carrying out Tortelli and Ruggieri's modification that the temperature does not exceed 70° to 80°, otherwise even pure olive oil will give a reaction. This author recommends the official Swiss modification as the most delicate and reliable; this process has been given with some modification on page 81, line 1.

Process Recommended.—Taking all things into consideration the process given above on page 81, line 1, will be found the most useful.

The Baudouin Reaction

The reaction which forms the basis of the Baudouin test was originally discovered by Camoin, but is generally known by the former name. This reaction is the production of a pink colour when the oil is shaken with a solution of cane sugar in hydrochloric acid. A convenient method of carrying out the test is as follows :

0·1 gram of finely-powdered sugar is dissolved in 10 c.c. of hydrochloric acid (S.G. 1·20), 20 c.c. of the oil to be tested is added, thoroughly shaken for a minute and allowed to stand. In the presence of sesamé oil the acid layer is coloured crimson.

The reaction has been studied at some length by Villavecchia and Fabris (*J.S.C.I.*, 1894, 13, 69), who considered that the reaction was caused by the furfural produced by the action of the hydrochloric acid on the cane sugar. They have accordingly suggested the use of this substance in place of cane sugar and proceed as follows :

Place 0·1 c.c. of a 2 per cent. furfural solution in a test-tube, add 10 c.c of the oil, and 10 c.c. of hydrochloric acid of specific gravity 1·19, shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 per cent. the aqueous layer will acquire a distinct crimson colour.

Weehuizen (*Analyst*, 1918, 43, 273) has stated that Van Ekenstein and Blanksma showed that β-hydroxy-*d*-methylfurfural, and not furfural, is formed by the action of hydrochloric acid on hexoses; later Blanksma states that the product is a α-hydroxy-methylfurfural. The substitution of furfural for the sugar in Baudouin's reaction for sesamé oil is therefore incorrect. This reaction is carried out by shaking a small amount of solid or liquid lævulose (cane sugar may be used) with 2 to 5 c.c. of a saturated alcoholic solution of hydrochloric acid for about one minute, adding an equal volume of the oil under examination, and again shaking vigorously for about one minute. A 5 per cent. solution of sesamé oil in olive oil gave a purple alcoholic layer on allowing to stand for five minutes; unadulterated samples gave a light red or greenish colour.

Gravenhorst (*J.S.C.I.*, 1924, 43, B183) considers that an amount of free chlorine much larger than that usually found in hydrochloric acid is required to affect the reaction. The exact strength of the hydrochloric acid is of much greater importance, an increase of 1 per cent. in the con-

centration above that specified giving a 25 per cent. deeper colour. Rancid sesamé oil gives as strong a colour as the fresh oil, but diluting the sesamé oil with rancid arachis, cotton seed, or soya bean oil or with rancid butter fat weakens the colour obtained and may even prevent the reaction altogether. The substances interfering with the reaction may be removed by treating the rancid oils with sodium hydroxide.

The idea of substituting some other sugar for cane sugar has been investigated by Fleig (*Analyst*, 1908, 33, 480), who finds that only lævulose, sucrose and invert sugar can be used—dextrose, maltose, etc., yielding either no colour or only the slightest trace. The same author has studied the effect of substituting a number of aromatic aldehydes for the sugar and finds that excellent colourations are produced (*Analyst*, 1908, 33, 480; 1909, 34, 285); he further shows that although sulphuric acid may replace the hydrochloric acid it is not in general so successful.

The Baudouin reaction is to some extent impaired when used with margarines containing added colouring substances which yield a red colouration when the sample is treated with hydrochloric acid (Arnold, *Analyst*, 1914, 39, 86), but this colouration does not interfere with Baudouin's test for sesamé oil if a small quantity of stannous chloride is added to the hydrochloric acid; about 0·1 c.c. of stannous chloride solution per 100 c.c. of the acid is sufficient for the purpose. The fat is dissolved in petroleum spirit and shaken with hydrochloric acid containing stannous chloride, the mixture being then heated by placing the test-tube for a short time in boiling water. When the red colouration has disappeared, the test is carried out in the usual way.

It has been shown by Gerber (*Analyst*, 1907, 32, 90) that fat extracted by chocolates may give the Baudouin reaction even when sesamé oil is entirely absent this being due either to the gum benzoin used in the glazing of the chocolates or the flavouring agents such as vanillin. Soltsien (*Analyst*, 1907, 32, 419) has confirmed this statement to a certain extent and states that such a reaction may be distinguished from the true sesamé oil in that the stannous chloride reaction is produced in the cold and not only after heating to 70° or 80°.

The test is not impaired by heating the oil to 250°; Heller (*J.S.C.I.*, 1923, 42, 896A) finds to the contrary and states, in opposition to Lewkowitsch, that the intensity is reduced by the action of animal charcoal, whilst Gravenhorst (*J.S.C.I.*, 1924, 43, B183), considers that refining with fuller's earth has the same effect. During hydrogenation the intensity of the reaction is gradually reduced until it almost completely vanishes, but, to a certain extent, it gradually returns on keeping the hydrogenated oil. All ordinary samples of sesamé oil give the reaction although some rancid oils have been found which give it with less intensity, whilst mixtures of small quantities of sesamé oil with quantities of other rancid seed oils sometimes fail to give the reaction altogether (Sprinkmeyer and Kreis, *Analyst*, 1908, 33, 100). Zimmermann (*J.S.C.I.*, 1912, 31, 442) has shown that the refining and deodourising of sesamé oil tend to reduce the intensity of the colour reactions. Kreis and Roth (*Analyst*, 1913, 38, 160) state that hydrogenated sesamé oil gives the Bellier reaction with nitric acid and resorcinol in benzene solution (2 c.c. of the oil shaken with 2 c.c. of a saturated solution of resorcinol in benzene and 2 c.c. of concentrated nitric acid) and also the hydrogen peroxide test (page 235). A slight reaction is sometimes given by olive oils which are perfectly genuine.

Prax (*J.S.C.I.*, 1921, 40, 778A) finds that if these normal olive oils are shaken with their own volume of 90 per cent. alcohol containing 10 per cent.

of ammonia, and then heated for five minutes on a water-bath to expel the alcohol and ammonia, the red colouration is not obtained when the Villavecchia test is applied.

Royer (*Analyst*, 1910, 35, 490) found that some samples of poppy-seed oil give slight positive reactions.

Method Recommended.—For all ordinary purposes it will be found quite sufficient to perform the simple test with cane sugar and hydrochloric acid as outlined above. Some of the modifications are perhaps more delicate, but extreme delicacy in such a test is not necessarily desirable, and in any case the slight advantages likely to be derived do not compensate for the additional labour involved.

CHAPTER VIII

PHYSICAL TESTS

Thermal Tests

When solid and liquid fats are mixed with certain reagents, such as free halogens or sulphuric acid, a large amount of heat is liberated and a considerable rise in temperature of the mixture takes place. The two substances which have been most widely used for this purpose are pure sulphuric acid and bromine, whilst sulphur chloride has been used to a less extent.

The method of working is quite simple, it being simply by mixing convenient quantities of the oil and the reagent and noting the rise in temperature. The actual experimental details are discussed below under the separate headings.

The Maumené Value.—Maumené's sulphuric acid test, which he first introduced in 1882, has been the subject of many investigations and the amount of work published on the subject is out of proportion with its importance. It was first introduced as a rapid sorting test, but there is no longer any great necessity for this as more accurate and almost equally rapid methods have been introduced, and if a thermal test is considered valuable for some particular purpose then the bromine thermal value, described below, will give better results. Olive oil is the only oil for which the test has ever been of any real value.

Archbutt (*J.S.C.I.*, 1886, 5, 304) laid down certain methods for carrying out the test, as he was able to show that the results obtained depended largely on the style of apparatus and particularly the strength of the acid used as is shown by the following table :

Table XIX.—Results of Maumené Test (Archbutt)

Kind of Oil.	Rise of Temperature observed with Acid containing per cent. of SO_4H_2						
	97·38.	96·71.	95·72.	94·72.	93·75.	92·73.	91·85.
	°C.	°C.	°C.	°C.	°C.	°C	°C.
Olive . . .	43·25 42·25	42	39	36·5	34·5	31	28 29·25
Rape . . .	63; 62	61	58	54	50·25	47	40·5; 43
Olive (impure)	48·5 48·5	47; 47·5	43·75 44·25	40·75 40·25	38·5; 39	35·5 35·5	32·5 32·5

In cases where a large rise in temperature is obtained various workers have suggested the dilution with an oil having a small value. Olive oil has been used by many, but Ellis (*J.S.C.I.*, 1886, 5, 150, 361) strongly recommends dilution with mineral oil, although Tortelli (*Chem. Zeit.*, 1909,

33, 126) has pointed out the errors to which this may lead and insists on the use of olive oil as a diluent. Where a diluent is used the Maumené number may be calculated in the following way: Mix one volume of the oil to be examined with two volumes of olive oil having, say, a Maumené figure of 45. If T is the rise in temperature observed then the Maumené figure for the oil will be given by

$$3\left(T-\frac{45\times 2}{3}\right)$$

It would appear, however, from the work of Kessler and Mathiason (*J.S.C.I.*, 1911, 30, 372) that the results do not follow the additive law in mixtures and that, therefore, this method will only give comparative results.

Thomson and Ballantyne (*J.S.C.I.*, 1891, 10, 234) suggest that, in order to overcome some of the sources of error, the temperature rise with the oil should be compared with that given by water under exactly similar circumstances. The ratio so obtained (multiplied by 100 to remove decimals) they term the specific temperature reaction. The method is carried out in the following way.

Place 50 grams of the oil into a small Dewar vacuum (a modified apparatus is suggested by J. W. Marden, *Analyst*, 1916, 41, 176; 1917, 42, 401) test-tube and adjust oil and sulphuric acid to approximately the same temperature. Run 10 c.c. of concentrated sulphuric acid into the oil from a pipette (time of delivery one minute) and stir with a thermometer to which may be attached a small paddle made of tin-plate. Continue the stirring until no further rise in temperature takes place and determine the rise in temperature (*a*). Now repeat the process using water at the same temperature and observe the rise in temperature in this case (*b*). The specific temperature reaction is then given by $\frac{100\ a}{b}$. It will be seen from the following table, due to Thomson and Ballantyne (*loc. cit.*) that this method almost entirely removes the discrepancies caused by variation in the strength of the acid.

TABLE XX.—RESULTS OF MAUMENÉ TEST (THOMSON AND BALLANTYNE)

Kind of Oil.	Sulphuric Acid of 95·4 per cent.		Sulphuric Acid of 96·8 per cent.		Sulphuric Acid of 99 per cent.	
	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.
Olive	36·5	95	39·4	95	44·8	96
Olive	..	..	39	94	43·8	94
Rape	49	127	..	..	58	124
Castor	34	88	37	89	..	..
Linseed	104·5	270	..	..	125·2	269
Water	38·6	100	41·4	100	46·5	100

The following results were obtained by Thomson and Ballantyne (*loc. cit.*) by their method (cf. Jenkins, *J.S.C.I.*, 1897, 16, 194; C. A. Mitchell, *Analyst*, 1901, 26, 169; Tortelli, *Analyst*, 1909, 34, 168):

Menhaden	306
Cod-liver	243–272
Seal	212–229
Whale	157
Linseed	320–349
Tung (Japanese)	330
Cotton-seed	163–170
Rape	125–144
Arachis	105–137
Olive	89–94
Castor	89–105
Neat's-foot	87
Sperm " oil "	93–100

It might be assumed that there is some relationship between the iodine value and the Maumené value. This is true to a certain extent, but as the factor varies from 1·83 in the case of olive oil to 1·15 in the case of castor oil it is obvious that the method can in no way be used as a substitute for the iodine value. In general the method will not be used for any purpose.

For the " Sulphuric Index," see olive oil, page 274.

The Bromine-Thermal Value.—The exothermic reaction between fats and bromine has been made use of by Hehner and Mitchell (*Analyst*, 1895, 20, 148) as a method for their examination in the following way :

Place 1 gram of the oil in a Dewar vacuum-jacketed test-tube and dissolve in 10 c.c. of chloroform and then add 1 c.c. of bromine at the same temperature from a pipette (the upper end of the pipette is fitted with a soda-lime tube and is best operated by means of a rubber teat). Stir the mixture with a thermometer to which may be attached a paddle made of tin-plate, and note the increase of temperature.

The method is rapid and the figure obtained multiplied by the factor 5·5 will, under certain circumstances, give an approximation to the iodine value. This is shown by the following table due to Hehner and Mitchell (*loc. cit.*):

TABLE XXI.—BROMINE-THERMAL VALUES (HEHNER AND MITCHELL)

Oil or Fat.	Heat of Bromination. °C.	Iodine Number.	
		Experiment.	Calculated.
Lard, No. 1	10·6	57·15	58·3
„ No. 2	10·4	57·13	57·2
„ No. 3	11·2	63·11	61·6
„ No. 4	11·2	61·49	61·6
„ No. 5	11·8	64·69	64·9
„ No. 6	11·8	63·96	64·9
„ No. 7	10·2	57·15	56·1
„ No. 8	10·4	57·80	57·2
„ No. 9	9·0	50·38	49·5
„ No. 10	11·0	58·84	60·5
„ 10 per cent. cotton-seed oil	11·6	64·13	63·8
Lard fatty acids	10·4	59·60	57·2
„ „ „	11·0	59·15	60·5
Mutton fat (kidney)	8·1	44·48	44·5
„ „ (flare)	7·6	39·70	41·8

TABLE XXI.—*Continued.*

Oil or Fat.	Heat of Bromination. °C.	Iodine Number.	
		Experiment.	Calculated.
Butter, No. 1	6·6	37·07	36·3
„ No. 2	7·0	38·60	38·5
„ and fatty acids	6·2	36·50	34·1
Almond oil	17·6	96·64	96·68
Olive oil	15·0	80·76	82·50
Maize oil	21·5	122·0	118·20
Cotton-seed oil	19·4	107·13	106·70
Castor oil	15·0	83·77	82·50
Linseed oils, No. 1	30·4	160·7	167·20
„ „ No. 2	31·3	154·9	172·00
Rape oil, No. 1	18·4	88·33	101·20
„ „ No. 2	17·6	77·2	96·80
Cod-liver oil	28·0	144·03	140·00
„ „ „	19·0	108·5	104·5
„ „ „ (commercial)	19·2	105·7	105·6
„ „ „ „	18·9	105·7	103·9

The variations observed in the case of linseed oil, rape oil and some others is doubtless due to the formation of substituted bromine compounds. The process has been considered by Jenkins (*J.S.C.I.*, 1897, 16, 194); L. Archbutt (*J.S.C.I.*, 1897, 16, 309); Wiley (*J.S.C.I.*, 1896, 15, 384); Gill and Hatch (*J.A.C.S.*, 1896, 18, 378); and J. W. Marden (*Analyst*, 1916, 41, 176).

The last observer expresses the value in calories per gram of oil. The following table gives his results together with the relationship of the values to the iodine values:

TABLE XXII.—RELATION OF BROMINE-THERMAL VALUES AND IODINE VALUES (MARDEN).

Oil or Fat.	Heat of Bromination.	Iodine Value found.	Iodine Value calculated. Factor, 0·846.	Deviation per cent.
	Cals. per grm.			
Sandalwood	274·0	270·0	232·0	−14·1
Raw linseed	206·0	172·5	174·2	0·98
Boiled linseed	204·6	169·0	173·0	2·36
Chinese Wood	150·0	156·0	127·0	−18·6
Maize	146·2	123·1	123·8	0·57
Sesamé	126·4	108·2	107·0	−1·12
Rape-seed	120·8	105·8	102·2	−3·4
Cotton-seed	117·0	101·7	99·0	−2·6
Sperm	109·0	93·4	92·2	−1·28
Castor (purified)	104·1	88·8	88·1	−0·79
„ (commercial)	102·2	87·5	86·5	−1·14
Arachis	102·2	83·2	86·5	3·96
Olive, I	100·7	84·0	85·2	1·43
„ II	96·6	80·0	81·7	2·12
„ III	95·4	80·3	80·7	0·5
Neat's-foot	83·0	68·7	70·2	2·2
Lard	79·3	68·6	67·2	−2·04
Mineral	nil.	..	..	..

The Sulphur Chloride Thermal Value.—The use of sulphur chloride in place of sulphuric acid was proposed by Fawsitt (*J.S.C.I.*, 1888, 7, 552). The method is carried out in a similar manner, and offers no particular advantages. It has not been examined at all extensively, and at the present time has probably fallen into entire disuse.

Miscibility Tests

The Valenta Test

The solubility of oils in acetic acid was first made use of by Valenta (*J.S.CI.*, 1884, 3, 643), who determined the solubility, not directly, but by means of what has been described as the critical temperature of dissolution, which is that temperature at which the oil and the acid first become completely miscible under standard conditions. This point is determined by heating the mixture until completely bright, and then allowing it to cool, and taking the temperature, well shaking all the time, at which the first permanent turbidity is obtained.

This test has been studied by various observers, notably by Allen (*J.S.C.I.*, 1886, 5, 282); Hoton, Thomson and Ballantyne (*J.S.C.I.*, 1891, 10, 233); Chattaway, Pearmain and Moor (*Analyst*, 1894, 19, 155); Jean, Fryer and Weston (*Analyst*, 1918, 43, 3); and Parkes (*Analyst*, 1918, 43, 82). These observers have shown that, although the test is of considerable value when proper precautions are adopted, serious discrepancies are likely to arise owing, firstly, to the use of acetic acid of varying strengths, and, secondly, to the influence of the presence of free fatty acids in the oil under examination.

The most complete examination of the method has been made by Fryer and Weston (*loc. cit.*), so that it is not necessary to deal with the earlier work at any length.

In order to overcome the difficulty of determining accurately the composition of the acetic acid used (a variation of 1 per cent. in the amount of water present makes a difference of nearly 30° in the reading obtained), these authors standardise the reagent by means of pure English expressed almond oil (cf. Jones, *Analyst*, 1894, 19, 151, who suggested butter) of known degree of acidity, and make a correction, based on a series of experiments, for the acidity of the oil under examination. The following is the method of working which they suggest:

Preparation of Reagents

(1) *Acetic Acid.*—Glacial acetic acid is allowed to solidify, and the crystals so obtained drained from adhering liquid at 15° C. They are then melted and the test with almond oil carried out as described below. Should the test give a figure varying from 70° to 90° the acid is suitable for use, although a figure as near to 80° as possible is desirable. If the figure obtained by the test is above 90°, a further freezing and draining of the crystals is necessary, whilst if below 70°, water is added to the acid until a suitable figure is obtained. The amount of water necessary is about 0·029 per cent. for each degree rise in temperature required.

The acid is preferably kept in a vacuum flask (of the kind readily purchased at a low figure nowadays). It will be then very unlikely to freeze

during the night in cold weather. If this is not available an ether bottle will suffice, but the acid must be melted when frozen, and will then probably change in value. A 2 c.c. pipette with a long stem is kept permanently immersed in the acid, being held tightly in a good cork, the open end kept closed by means of a piece of rubber tube provided with a cap of solid glass rod, the whole forming a close cover. It is thus unnecessary to suck the acetic acid into the pipette for measurement, and accession of moisture from this cause is avoided. Parkes (*Analyst*, 1918, 43, 82), suggests the employment of a proportion of butyric acid to prevent freezing; he suggests about 10 per cent.

(2) *Standard Oil.*—This should be English expressed almond oil (obtainable from Stafford Allen) which should be kept in a well-corked bottle, and the acidity determined at intervals. The figure obtained is corrected for acidity as described below.

(3) *Preparation of the Oil.*—The oil must be absolutely free from moisture or the results will be useless. This condition is best brought about by filtering the warm oil through thick filter-paper. Fryer and Weston state that the oil should further be placed in a test-tube immersed in boiling water, and that a thick wad of cotton-wool should then be forced to the bottom of the tube by means of a stout wire plunger; in this way all traces of moisture will be removed.

The Test

A test-tube is used of such diameter that the bulb of the thermometer is completely covered by 4 c.c. of liquid. The thermometer is inserted tightly into a cork fitting to the test-tube, a small groove being cut in the side of the cork for escape of hot air. A graduation mark is made on the test-tube with a diamond or file at 2 c.c. from the bottom. Pour the oil into the tube up to the 2 c.c. mark at the temperature of boiling water (Fryer and Weston have shown that the results are not affected by *slight* variations in the proportions of the oil and solvent) and measure in also 2 c.c. of the acid at about 20° by means of the pipette. Insert the thermometer and heat, whilst shaking carefully, over a naked flame until the mixture clears. Then allow to cool slowly, shaking all the time, and take the temperature at which the first signs of turbidity appear. The acid value of the oil is determined, and the experimental figure corrected for this, and also for the reading actually obtained at the same time with the sample of almond oil as described below. (This last precaution is necessary as the acetic acid reagent readily changes in strength on keeping.)

Fryer and Weston carry out the test with two thermometers, one having a small bulb and reading to 0·5°, and the second having a large bulb and reading to 0·1°. They first carry out the test as described above, using the small bulb thermometer. Then they repeat the determination, using the large bulb thermometer (graduated to 0·1°), but this time place the tube in water heated to about 5° above the temperature found in the former determination and shake until clear. The tube is then allowed to stand immersed in the hot water until the faintest sign of turbidity appears, when the exact temperature is noted. This refinement will give accurate results suitable for exact work, but will hardly be necessary for routine examinations when, in general, the single determination will suffice.

Calculations

(1) *Correction for Acidity.*—The correction for acidity of the oil should first be made. Ascertain, by reference to the following table, the correction for 1 per cent. acidity for the class of oil under test, multiply this by the acidity found and *add* the result to the temperature figure obtained.

TABLE XXIII.—INFLUENCE OF ACIDITY OF OILS ON VALENTA FIGURES

Class of Oils.	Typical Oil employed.	Fall in Turbidity Temperature. Degrees per 1 per cent. Acidity (as Oleic).
Marine	Whale	1·90
Drying	Linseed	1·85
Semi-drying	Cotton-seed	1·77
Non-drying (except rape and castor)	Almond	2·27
Vegetable fats (except coconut group)	Palm	2·10
Rape-oil group	Rape	2·23
Coconut oil and palm kernel	Coconut	1·73
Animal fats (except butter fat)	Lard	2·15
Milk fats	Butter fat	1·41

Note.—If the class of the oil is unknown, a figure of 2·0 may be allowed in all cases, but the acidity of the oil, for this test, should be preferably low.

(2) *Correction for Acetic Acid.*—The figure given by the acetic reagent with the standard almond oil must, where it differs from 80°, be corrected by means of the following formula:

$$V = t + (80 - t'),$$

where V = " true Valenta."
t = temperature obtained with oil tested, corrected for acidity.
t' = temperature with standard oil and the same acid (correcting for acidity if necessary).

Note.—If the standard almond oil is not *neutral*, the acidity must be ascertained, and the correction made in all cases.

(3) *Typical Results.*—Fryer and Weston suggested that the final figure should be put into the form

$$\frac{V \times 10}{80}$$

which gives a figure in the neighbourhood of 10·0, and which shows by inspection that the necessary corrections have been made.

The results obtained by these authors are set out in the following table:

TABLE XXIV.—TYPICAL RESULTS OF VALENTA TESTS (FRYER AND WESTON)

Oil or Fat.	Acidity per cent. (as Oleic).	Valenta Number Acetic Acid. t.	Standard Test Almond Oil. (t').	Adjustment Factor for Acidity.	True Valenta $V=t+(80-t')$.	$\frac{V \times 10}{80}$.
Perilla	5·5	19·0	73·5	1·85	35·7	4·5
Linseed	2·0	39·5	76·0	1·85	47·2	5·9
Tung	0·9	38·3	73·5	1·85	46·5	5·8
Soya bean	1·0	61·5	90·0	1·85	53·3	6·7
Niger	1·2	45·3	73·5	1·85	54·0	6·7
Sunflower	2·2	52·7	73·5	1·85	63·2	7·9
Maize	2·8	73·2	90·0	1·77	68·2	8·5
Cotton	0·1	69·5	90·0	1·77	59·7	7·5
Sesamé	4·0	73·0	90·0	1·77	70·0	8·7
Rape	0·6	109·0	80·0	2·23	110·3	13·8
Almond	0·9	78·3	80·0	2·27	80·3	10·0
Arachis	1·1	95·8	90·0	2·27	88·3	11·0
Olive (1)	0·7	70·0	80·0	2·27	71·6	9·0
Olive (2)	1·8	72·5	80·0	2·27	76·5	9·5
Olive (3)	3·6	68·0	80·0	2·27	76·2	9·5
Cacao butter	2·9	88·0	80·0	2·10	94·0	11·7
Chinese vegetable tallow	6·9	69·8	90·0	2·10	74·3	9·3
Palm oil	0·1	89·8	76·5	2·10	93·5	11·7
Japan-wax *	118·7	37·0	88	2·10	(68 ?)	..
Lard	0·9	82·0	76·5	2·15	87·5	10·9
Tallow	0·1	102·0	90·0	2·15	92·2	11·5
Butter fat	1·9	45·3	90·0	1·41	38·0	4·7
Coconut	0·0	13·5	81·5	1·73	12·0	1·5
Palm-kernel fat	0·0	25·5	81·5	1·73	24·0	3·0
Coconut (2)	1·6	..	..	..	..	..

The following papers may be consulted: C. Grimme (*Analyst*, 1914, 39, 216, 434); J. R. N. van Kregten (*J.S.C.I.*, 1920, 39, 305A); G. Fascetti (*J.S.C.I.*, 1922, 41, 912A); A. O. A. C. (*Analyst*, 1923, 48, 224); but the information contained therein is largely covered by the work of Fryer and Weston given above.

The Crismer Test

The use of alcohol in a similar manner to that of acetic acid in the Valenta test was first suggested by Crismer (*Analyst*, 1895, 20, 209), and has been widely adopted for some purposes on the Continent. The method has been discussed by several authors such as Cesaro, Herlant, Asboth and Stewart (cf. *J.S.C.I.*, 1896, 15, 300, 562), but the work of Fryer and Weston has replaced that of the earlier authors. Fryer and Weston (*Analyst*, 1918, 43, 3) use a mixture of equal volumes of amyl alcohol and industrial methylated spirits (92 per cent.) adding sufficient water—about 0·11 per cent. for each 1° rise in the observed temperature required—to bring the experimental result with almond oil to 70° after making the allowance for the acidity of the latter.

* Acidity too high for calculation.

For every 1 per cent. of acidity, as oleic acid, the standard temperature must be lowered by 2·07°. Thus, in the case of almond oil of acidity 1·5 per cent., the alcohol is adjusted to give a turbidity temperature of 66·9°. The great advantage of this reagent over that of Valenta (acetic acid) is that it keeps for a considerable length of time without changing.

The test may be carried out in exactly the same manner as is described on page 90, for the acetic acid reagent, whilst the acidity of the oil may be readily determined on the mixture after completion of the test. The influence of the acidity of the oils may be seen from the following table due to Fryer and Weston:

TABLE XXV.—INFLUENCE OF ACIDITY OF OILS ON TURBIDITY FIGURES, (AMYL-ETHYL-ALCOHOL REAGENT) (FRYER AND WESTON)

Class of Oils.	Typical Oil employed.	Fall in Turbidity temperature. Degrees per 1 per cent. Acidity (as Oleic).
Marine	Whale	1·95
Drying	Linseed	2·05
Semi-drying	Cotton-seed	2·03
Non-drying (1)	Almond	2·07
Non-drying (2)	Rape	1·61
Vegetable fats (except coconut group)	Palm	1·72
Coconut group	Coconut	2·01
Animal fats (except butter fat)	Lard	2·13
Butter and Milk fats	Butter fat	1·54

Note.—If the class of the oil is unknown, a figure of 2·0 may be allowed in all cases, but the acidity of the oil, for this test, should preferably be low.

The following table due to the same authors gives the results likely to be obtained for different classes of oil:

TABLE XXVI.—RESULTS OF CRISMER TESTS FOR DIFFERENT CLASSES OF OIL (FRYER AND WESTON)

Oil or Fat.	Acidity per cent. (as Oleic).	Crismer Value (mod.).	Adjustment Factor for Acidity.	True Talue.
Perilla oil	5·5	49·0	2·05	60·3
Linseed oil	2·0	58·3	2·05	62·4
Tung oil	0·9	74·0	2·05	75·8
Soya-bean oil	1·2	65·0	2·05	67·0
Niger oil	2·2	57·5	2·05	60·0
Sunflower oil	2·2	59·5	2·05	64·0
Maize oil	2·8	62·5	2·03	68·2
Cotton oil	0·1	65·0	2·03	65·2
Sesamé oil	4·0	60·5	2·03	68·1
Rape oil	0·6	82·3	1·61	83·3
Almond oil	0·9	68·2	2·07	70·1
Arachis oil	1·1	72·0	2·07	74·3

TABLE XXVI.—*Continued.*

Oil or Fat.	Acidity per cent. (as Oleic).	Crismer Value (mod.).	Adjustment Factor for Acidity.	True Value.
Olile oil (1)	0·7	67·8	2·07	69·2
„ „ (2)	1·8	65·5	2·07	69·2
„ „ (3)	3·6	61·5	2·07	69·0
Cacao butter	2·9	71·0	1·72	76·0
Chinese vegetable tallow.	6·9	54·0	1·72	65·9
Palm oil	0·1	68·0	1·72	68·2
Japan-wax *	18·7	44·0	1·72	76·1
Lard	0·9	70·8	2·13	72·7
Tallow.	0·1	72·5	2·13	72·7
Butter fat	1·9	43·0	1·54	46·0
Coconut	0·0	34·0	2·01	34·0
Palm kernel	0·0	40·0	2·01	40·0
Coconut (2)	1·6	30·0	2·01	33·2

Other information on the Crismer test is given by A. J. J. Vandevelde (*J.S.C.I.*, 1911, 30, 755; *Analyst*, 1921, 46, 243); H. Duper (*J.S.C.I.*, 1911, 30, 907); Hoton (*J.S.C.I.*, 1912, 31, 397); Davidsohn and Wrage (*J.S.C.I.*, 1915, 34, 722); Stewart (*J.S.C.I.*, 1918, 37, 668A); J. R. N. Van Kregten (*J.S.C.I.*, 1920, 39, 305A); L. Vandam (*Analyst*, 1920, 45, 19).

Various other substances such as acetone, aniline and alcohol, phenol, benzene, dimethylsulphate (Harrison and Perkin, *Analyst*, 1908, 33, 2), and liquid sulphur dioxide (*J.S.C.I.*, 1922, 41, 581A), have been suggested as suitable solvents for modified turbidity methods, but up to now the results obtained have not been superior to those recorded above.

Miscibility Curves

The principle of miscibility curves was first suggested by Louise and Sauvage (*Analyst*, 1907, 34, 365), who obtained a series of turbidity temperatures, using acetone, by means of the following method, and plotted the results in the form of a curve:

A weighed quantity of the oil is mixed with 20 c.c. of acetone in a tube closed with a cork, through which a thermometer is passed. The mixture is then either heated or cooled, as required, until a point is obtained at which the turbidity just disappears. This is called the mixing-point. Other weighed quantities of the oil are treated in the same way, and from the observations obtained a curve is plotted out, the temperature being set off against the weight of oil. The quantity of oil employed should lie between 15 and 30 grams. With more than 30 grams of oil to 20 c.c. of acetone, the mixture becomes very viscid, so that the temperature is not the same throughout the mass.

The curve so obtained is characteristic for each oil and is said to be a means not only of distinguishing one oil from another, but also of detecting the presence of adulterants in known oils. Louise has continued his work on this subject (*J.S.C.I.*, 1909, 28, 892; 1910, 29, 438; 1911, 30, 556) with cod-liver oil and other oils and reports useful results. He has applied the same method to the examination of butter (*J.S.C.I.*, 1911, 30, 965) and

* Acidity too high for calculation.

butter substitutes and in this connection he uses a cylindrical bath containing concentric chambers, the outer of which is closed with the exception of two small openings for the escape of vapour and the introduction of a thermometer. This chamber is charged with heavy lubricating oil (" valvoline "), whilst the inner chamber is filled with ordinary petroleum oil. 10 grams of the melted and dried fat and 10 c.c. of the " typical " petroleum oil are placed in a large test-tube, which is closed with a cork through which passes a thermometer, and is placed in the inner chamber. The " typical " petroleum oil should be such that when 20 c.c. thereof are mixed with 10 c.c. of absolute alcohol the turbidity temperature is 4·9°, and with 5 c.c. of alcohol, 4·0°. Increasing quantities of aniline are then introduced into the tube, the turbidity temperatures determined and the miscibility curves plotted. 5 c.c. of the aniline should give a reading of 69° when mixed with 10 c.c. of the typical petroleum oil, and 10 c.c. a reading of 72°.

The method has been adapted to cacao butter by Marange (*J.S.C.I.*, 1923, 42, 840A) and by Rosset, Marange and Vinter (*Analyst*, 1924, 49, 91) all of whom use aniline-alcohol mixtures. These authors state that with a suitable liquid, such as pure aniline, which may be identified by its miscibility curve with a well-defined liquid like 50 per cent. aqueous alcohol (1) pure cacao butters yield virtually identical miscibility curves, the extreme differences of temperature being 2·7°; (2) with the exception of illipé butter, the common adulterants of cacao butters do not exhibit the phenomenon of miscibility; and (3) the presence of minimum proportions of such adulterants in cacao butter may be detected by means of the temperatures of reciprocal miscibility.

The method will doubtless receive extended trial by various workers and may under suitable conditions be found to yield valuable results.

Melting-Point

Although normally quite a simple process the determination of the melting-point is, in the case of fats, one of considerable difficulty. The determination of an exact melting-point is impossible on account of the fact that, firstly, because of their nature fats do not melt sharply and, secondly, the figure obtained depends very largely on the conditions of the experiment.

The difficulty is further increased by the property possessed by triglycerides, which is known as the " double melting-point." The higher of the two melting-points is the one usually taken to be the " correct " one; it is the figure obtained with the glyceride in the crystalline condition, a condition which is reached only when the substance has remained in the solid condition for some hours. The lower melting-point is probably given by an amorphous or unstable modification. The phenomenon is well shown in the case of tristearin, which has a normal melting-point of 71°, but if the melting-point be determined immediately after fusion and resolidification it will be found to be 55°. According to Bömer (*Analyst*, 1907, 32, 357) the lower melting-point is the temperature at which the labile modification changes into the stable form. Le Chatelier and Cavaignac (*J.S.C.I.*, 1913, 32, 296), from an investigation carried out with " végétaline " (a coconut oil preparation) and stearin, conclude that the change of state of fats at their melting-points is strictly reversible, as in the case of chemical compounds generally, but that it is characterised by extreme slowness. Various aspects of this question have been studied by de Visser (*J.S.C.I.*, 1898, 17, 853), Carlinfanti and Levi-Malvano (*J.S.C.I.*, 1909, 28, 1318), and by R. Kremann and his co-workers (*J.S.C.I.*, 1912, 31, 1040; 1914, 33, 928, 929). Cf.

also Grün (*Berichte*, 1912, 45, 3691), Smits and Bokhurst (*Proc. K. akad. Wetensch. Amsterdam*, 1912, 15, 681), and E. Twitchell (*Analyst*, 1914, 39, 448). A. Eisenstein (*J.S.C.I.*, 1920, 39, 663A).

The important point to remember for practical work is that the melting-point of fats should not be taken for some time after they have been allowed to solidify. In the case of some fats, such as cacao butter, several days are necessary, in other cases twenty-four hours will suffice, but in order to be on the side of safety as much time as possible should be allowed. Where time is an important item a few hours on ice may be substituted for a longer time at the ordinary temperature with little liability of error.

Frequently results are given under two headings, firstly, the point of incipient fusion, which is the temperature at which the fat is just becoming liquid, whilst still retaining solid particles, and, secondly, the point of complete fusion, which is the temperature at which the fat becomes completely transparent. The latter temperature is the one usually reported where no descriptive details are mentioned, but it is always wise to refer to the actual process that has been adopted when recording results.

Methods for the Determination of Melting-Point

1. *The Capillary Tube Method.*—A small quantity of the fat is placed in a thin-walled capillary tube (made by softening in the Bunsen flame a piece of ordinary glass tubing about 5 mm. in diameter and drawing it out : it should not be too narrow) closed at one end. The tube is attached to the bulb of a thermometer by a small rubber band (easily made by cutting about $\frac{1}{16}$th of an inch from a piece of ordinary $\frac{3}{16}$th rubber tubing) so arranged that the part of the tube containing the substance is at the middle point of the bulb. The thermometer is then placed in some suitable liquid bath (heavy liquid paraffin or glycerin serve well), the end of the capillary tube being above the level of the liquid, provided with a stirrer, preferably mechanical, and gently heated by means of a very small flame. The temperature should not rise more than about 1° per minute when the neighbourhood of the melting-point is reached. The appearance of the fat is carefully watched and the temperatures noted when the changes in consistency take place (cf. M. Monhaupt). An elaborate apparatus for the routine determination of melting-points has been suggested by Blichfeldt and Thornley (*Analyst*, 1921, 46, 180), Christomanos (*J.S.C.I.*, 1890, 9, 894), Le Sueur and Crossley (*J.S.C.I.*, 1898, 17, 988).

2. *The Thermometer Bulb Method.*—This method, which consists in coating the bulb of a thermometer with a thin layer of fat and noting the temperature at which a drop of liquid fat forms at the bottom of the bulb, was originally suggested by Pohl and has been examined by Finkener, Ubbelohde, T. Redwood, Meldrum and Knapp. The difficulty attaching to the method is that of obtaining a uniform layer on the thermometer bulb and considerable inaccuracies may be caused by this means. The method has been examined at some length by Meldrum (*J.S.C.I.*, 1913, 32, 1077), who states that the essential point is the uniformity with which the thermometer bulb is coated with the fat in sufficient quantity to form two drops. If the first falling drop appears opaque the coating is too thick and the thermometer should be heated or cooled 5° to 10° and its bulb recoated by a rapid dip into the fat. It is also necessary to remove the fat from the apex of the bulb by means of filter-paper; otherwise the readings will be too high. In the case of very soft mixtures it is advisable to cool the bulb to 0° or −5° and then to make a rapid dip. Too thin a film of fat

will cause the drop to form too slowly and the M.Pt. to be too high. A suitable apparatus for the determination is a test-tube, 7 in. by 1 in., which is passed through a bung in a beaker about 7 in. by 3 in. The thermometer with the attached fat is fixed centrally in the test-tube, whilst a glass stirrer is moved continually up and down in the water round the outside of the tube. The speed of heating should be at about the rate of 1° in two minutes, and the larger the bulb of the thermometer the more gradually should the temperature be raised.

A modified form which gives good results, and which leads to accurate results, is suggested by Knapp (*J.S.C.I.*, 1915, 34, 1121), who proceeds as follows:

Very fine scrapings are taken with the point of a knife over a representative surface of the material. These fine scrapings are transferred with as little injury as as possible to the bulb of the thermometer. They should cover less than one-half of the bulb. Under these conditions one can plainly see when the sharp outline of the scrapings begins to soften, and also when the fat is completely transparent.

An alternative method of carrying out this test is as follows: An amount of mercury sufficient easily to cover the bulb of the thermometer used, is placed in a small basin which is in turn put into a beaker containing water which can be heated gradually. A small quantity of the fat, in small shavings, is placed on the surface of the mercury. On heating the water in the beaker, a point will be reached at which the fat spreads over the surface of the mercury. Slow heating is essential for the accuracy of this method, which is not so good as that of Knapp above.

3. *Platinum Loop Method.*—This method is carried out (*Analyst*, 1917, 42, 29), in the following manner:

To the thermometer employed is attached a platinum wire of a thickness of 0·3 to 0·4 mm., the free end of which is formed into a loop of 8 to 9 mm. diameter. The wire is attached in such a manner that the loop assumes a vertical position immediately in front of, but not touching, the mercury bulb. The fat to be examined is melted at a gentle heat, and when it is almost cool enough to solidify, the platinum loop is dipped parallel to the surface into the liquid and quickly withdrawn, leaving a thin film of fat, completely filling the loop. This is allowed to cool for an hour,* the wire attached to the thermometer, which is then immersed in a wide-necked glass flask of about 250 mm. capacity, filled with distilled water, which is slowly heated on an asbestos card, until the film of fat in the platinum loop becomes completely transparent just before breaking up. The temperature of complete transparency is the melting-point of the fat.

Method Suggested.—The simplest method, and one which gives results as accurate as can be expected from the nature of the fats themselves, is that of Knapp. In some cases where it is necessary to confirm results obtained by this method, the capillary-tube process may be used. A note should be made of the temperatures of incipient fusion and of complete fusion.

Melting-Points of the Mixed Fatty Acids.—In general, the melting-points of the mixed fatty acids are more easy to determine with accuracy. The determination may be carried out either by Knapp's method, or by the capillary-tube method, and no difficulty is usually encountered.

* Cf. page 96.

Solidifying Points

A. Solidifying Point of Mixed Fatty Acids. Titer Test

When the mixed fatty acids in the molten condition (and to a lesser degree the oils themselves) are allowed to cool, and so commence to solidify, the latent heat of fusion is liberated, so that the rate of cooling will be considerably reduced at the point of solidification, and frequently a considerable rise in temperature is observed. This observation forms the basis of the titer test, which will now be described. In order that concordant results may be obtained by various workers it is most important that the test be carried out under standard conditions, and to this end numerous suggestions have been made by various authors. The method which has received most general acceptance is that of Dalican, which may be carried out in the following way:

Obtain the fatty acids from 50 grams of fat as described on page 44, allow the fatty acids to solidify and to stand overnight in a desiccator. Melt the substance carefully and pour as much into a test-tube 16 cm. long by 3·5 cm. wide, as will fill the tube more than half full. Fasten the tube by means of a cork into a wide-mouthed bottle 10 cm. wide, 13 cm. high and then place a thermometer (graduated in 1/10° from −5 to 60° C. having a mercury bulb about 3 cm. long and 6 mm. in diameter, and carefully calibrated) in the fatty acids, so that the bulb is in the centre of the mass, by means of a cork held in the mouth of the test-tube. Observe carefully when turbidity commences, or crystals commence to separate out, and then stir the mass with the thermometer in one direction three times, and then in the contrary direction three times, and then continuously without touching the sides of the test-tube. The temperature is then carefully watched. It will be found at first to fall regularly (readings may be taken every half-minute, and plotted if so desired), and then a sharp rise will take place, after which it will remain stationary and then commence to fall again. The highest point of the rise is taken as the titer. Duplicate results should agree to within 0·1°.

The following results have been obtained by Lewkowitsch (*Oils, Fats and Waxes*, Vol. I), from the examination of a large number of samples of oils of the kind named:

Table XXVII.—Titer Tests of Mixed Fatty Acids (Lewkowitsch)

Class of Oils.	Kind of Oil.	Titer Test. °C.
Drying oils	Linseed	20·6
	Tung	37·2
	Hemp seed	16·6
	Safflower	16
	Soya bean	21·2
	Poppy seed	16·2
Semi-drying oils	Cotton seed	32·0–35·2
	Maize	19·0
	Sesamé	23·8
	Croton	19·0
	Curcas	28·6
	Rape	13·6

TABLE XXVII.—*Continued.*

Class of Fat or Wax.	Kind of Fat or Wax.	Titer Test. °C.
Non-drying oils	Peach kernel	13·5
	Almond	11·8
	Arachis	29·2
	Kœme	38·8
	Olive	17·2–26·4
	Ben	37·8
Marine animal oils	Japanese sardine	28·2
	Cod-liver	13·9–24·3
	Seal	15·9
	Whale	23·9
Terrestrial animal oils	Sheep's-foot	21·1
	Horse's-foot	28·6
	Neat's-foot	26·5
Vegetable fats	Chaulmoogra oil	39·6
	Pongam oil	44·4
	Laurel oil	15·1
	Carapa oil	34·9
	Margosa oil	42·0
	Niam fat	42·5
	Mowrah-seed oil	40·3
	Palm oil	35·9–45·6
	Macassar oil	51·6–53·2
	Sawarri fat	47·0
	Nutmeg butter	36·0
	Shea butter	53·8
	Cacao butter	48·3–49·6
	Chinese vegetable tallow	45·2–53·4
	Palm-nut oil	20·5–25·5
	Coconut oil, commercial	22·6–25·2
	Coconut oil, Cochin	25·2
	Japan-wax	59·4
Animal fats	Horse fat	33·7
	Horse-marrow fat	38·6
	Lard	42·0
	Beef tallow	38·3–46·3
	Mutton tallow	41·5–48·3
	Beef marrow	38·0
Liquid waxes	Sperm oil	11·9
	Arctic sperm oil	8·6

The Committee of Analysts appointed by the Ministry of Food in 1918 state that in cases where it is desirable to determine titer the method to be adopted is that prescribed by the Seventh International Congress of Applied

Chemistry. This method is given in full in J. Lewkowitsch's *Chemical Technology of Oils and Fats*, fifth edition, 1913, Vol. I.

For convenience this description is given here :

"(*a*) A clear glass cylindrical vessel having an inside measurement 9 cm. high and 2·75 cm. diameter, and sides about 0·30 cm. thick, slightly rounded at the bottom and provided at the top with a glass lip or ebonite flange.

(*b*) An outer vessel of clear glass (13 cm. deep and 10 cm. wide), for the protection of the inner cylinder from draughts, etc.

(*c*) An ebonite or wooden cover (not metal or other good conductor of heat), with a hole in the centre and slightly depressed flange on which to hang the flange of the inner cylinder.

(*d*) Two small pins to keep the cylinder in position.

(*e*) An accurate thermometer graduated from about $-5°$ to about 70 in $\frac{1}{5}$th of a degree. The size of the bulb to be as nearly as possible 2·5 cm. in length and 0·60 cm. in diameter.

(*f*) An upright pillar provided with :

(*g*) An arm from which to suspend the thermometer, and fastened into :

(*h*) A stout base or stand of wood, hollowed slightly to receive the larger glass vessel and keep it in position.

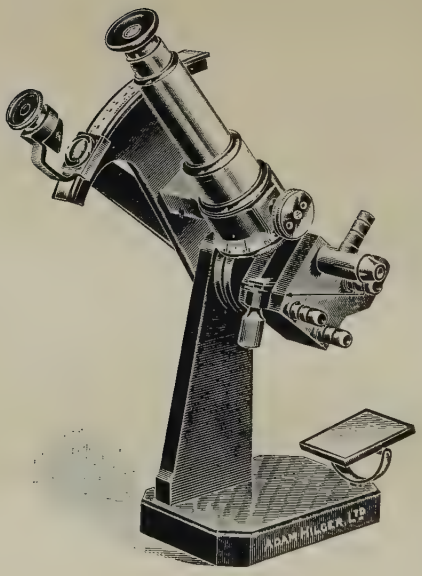
For the convenience of raising the apparatus, if necessary, so as to bring the top of the mercury in the thermometer on a level with the eye, the apparatus may, if required, have the wooden stand attached to a sliding tube fixed over the upright rod and movable by the screw. In this case there will be required a further foot to support the whole.

The Committee agreed, since brokers, merchants and others find it necessary for commercial purposes (such as tendering for sale, the removal of goods from quay, shipping, etc.) to have the " titer test " reported as quickly as possible, that in urgent cases the author's direction, viz., to allow the fatty acids to solidify and to stand overnight under a desiccator (see p. 98) need not be insisted upon, especially so, as Frank Tate urged that in his own experience no difference in results was obtained. Inasmuch as the author had found, not infrequently, that lower results were obtained when the fatty acids were tested immediately after they had been liberated, an experience which is confirmed also by other observers, the compromise arrived at by the decision of the Committee should be used in cases of urgency only."

B. Solidifying Point of Fats

The solidifying point of fats may be determined in the same apparatus as that in which the titer test is determined. The rise in temperature, however, frequently does not take place and a slowing down in the rate of cooling is all that is noticed. It follows then that the method is not so accurate as is the titer test, yet on account of the ease and rapidity with which it can be determined it is sometimes of considerable value.

Polenske (*Analyst*, 1907, 32, 382; 1908, 33, 476), who uses the difference between the melting and solidifying points of a fat as a means of detecting adulteration, obtained the solidifying-point as that point at which two narrow black lines (2 mm. long, 0·5 mm. thick and 0·25 mm. from each other) drawn on the further side of the tube no longer appear as separate lines. This method would not appear to be as accurate as the one given above.



[*By permission of Adam Hilger & Co. Ltd.*

FIG. 1.—Zeiss Refractometer

Facing p. 101

The Index of Refraction

Many instruments are now on the market by which the index of refraction of various substances can be rapidly determined. There would seem to be no useful purpose in describing these instruments at length in this place more particularly as complete details are always supplied with each instrument.

For technical work refractometers reading to more than the fourth decimal place are unnecessary and, inasmuch as a higher degree of accuracy requires considerably more care and time, undesirable. For most purposes the Abbé refractometer, which reads directly to four decimal places, is the best instrument, although the butyro-refractometer has several advantages in that it is less expensive, requires no setting and is somewhat more delicate; most oils have refractions which lie on the scale of this instrument, but it is not of much value for other substances. The butyro-refractometer gives its readings on an arbitrary scale. These readings may be transferred to indices of refraction, and *vice versa*, by means of the conversion table given on page 486. The setting of the butyro-refractometer is discussed by Liverseege and Singleton (*Analyst*, 1921, 46, 93).

As has already been explained on page 6 the temperature adopted for the determination of the index of refraction is 40°—where slight differences of temperature are used, in order to save setting the instrument exactly at 40°, a correction may be made by adding 0·00037 to the determined value for each degree that the temperature is too high and *vice versa*.

The temperature of the instrument is fixed by means of a constant stream of water at known temperature. The apparatus to obtain this is usually expensive, the following apparatus, however, has been found by the author to be quite satisfactory; it costs a few shillings :

An enamelled camp kettle of about 4 litres capacity, fitted with a lid, and about 15 feet of $\frac{1}{4}$ inch *drawn* brass tubing are required. The tubing is rolled up into a spiral of sufficient size to fit into the kettle, and two small holes are bored in the lid through which the ends of the spiral are passed—one end being connected with the refractometer and the other to a constant head of water. The water, after it enters the heater, should have an entirely upward course, this being so arranged to prevent the accumulation of air bubbles.

A refractometer of a different type constructed by Amagat and Jean was in use up to a few years ago. This instrument, known as the oleo-refractometer, was one in which the oil to be examined was compared with a standard oil supplied by the makers and the result expressed in " degrees " with either a positive or negative sign. In order that older figures in the literature obtained by this instrument may be compared with indices of refraction the following table (p. 102) showing the relationship between the two may be found of value.

A very simple method of obtaining the refractive index of a sample of oil has been suggested by H. S. Simms (*J.S.C.I.*, 1921, 40, 706A). In this method the oil is drawn into a bulb, 0·5 in. in diameter, having a capillary above and below it; the lower capillary is then sealed and the bulb full of oil is immersed in an oil of known refractive index contained in a wide test-tube. The bulb is raised and lowered while looking through it at a distant object; if the image rises as the bulb is raised and sinks as the bulb is lowered, the refractive index of the oil is less than that of the standard oil in the test-tube. Similarly, if the bulb is filled with an oil having a greater refractive index than that of the standard, the image sinks when the

bulb is raised and rises when the bulb is lowered. By testing the bulb in a series of oils of different but known refractive indices, the value for the oil under examination may be found within 0·0005 of the true value.

TABLE XXVIII.—COMPARISON OF INDICES OF REFRACTION

Refractive Index. 15°.	Oleo Refractometer Refractive Figure. 22°.	Refractive Index. 15°.	Oleo Refractometer Refractive Figure. 22°.
1·4668	−17	1·4734	11
1·4673	−15	1·4744	15
1·4678	−13	1·4770	26
1·4684	−10	1·4784	32
1·4694	−6	1·4790	34¾
1·4698	−4	1·4800	39
1·4700	−3½	1·4805	41
1·4708	0	1·4810	43
1·4713	2	1·4822	48
1·4720	5	1·4832	52½
1·4725	7	1·4840	56
1·4729	8½	1·4844	57½
1·4730	9		

It is quite possible to purchase oils of known refractive index commercially, so that the method may be found useful, if tedious, by those who do not possess a refractometer.

The following papers may be consulted for the special points with which they deal:

"The Refraction Constants of Vegetable Oils." J. Kliment, *J.S.C.I.*, 1911, 30, 292.

"The Relation of the Refraction of the Fatty Acids to that of the Oil from which obtained. W. B. Smith, *J.S.C.I.*, 1912, 31, 139.

"The Relation between the Chemical Constitution and Refractive Index of Fats." C. Chéneveau, *J.S.C.I.*, 1918, 37, 64A.

"The Bromine Refraction Value of Fats." R. Biazzo, *J.S.C.I.*, 1924, 43, B478.

VISCOSITY

When any liquid is allowed to flow through a narrow tube the velocity will not depend entirely on the "head" of liquid which produces the flow as the liquid itself shows more or less resistance to the motion. Findlay states that all parts of the liquid do not move through the tube with the same velocity, but the layers next the sides of the tube move more slowly than the middle layers. There is thus a shearing, or a movement of the different layers past one another in the direction of flow; and this displacement of the different layers relatively to one another is opposed by the internal friction or viscosity of the liquid. We can, therefore, regard the liquid as made up of a number of concentric tubes sliding past one another like the tubes of a telescope.

When the liquid is moving through the narrow tube, there will be a constant difference in velocity between the different tubes, of which we

have regarded the cylinder of liquid made up, and it has been found that the force per unit area which is necessary to maintain this condition is proportional to the difference of velocity, v, of two adjacent tubes (or their relative velocity of displacement), and inversely proportional to their distance, x, apart, i.e.:

$$\text{Force} = n \times \frac{v}{x}$$

where n is a constant known as the *coefficient of viscosity*. When the velocity of displacement of two layers is equal to the distance between the layers ($v = x$), the force per unit area becomes equal to the coefficient of viscosity. This gives the definition of the latter quantity. It may be defined as the force required to move in opposite directions two surfaces of a liquid 1 sq. cm. in area, and 1 cm. distant with a velocity of 1 cm. per second.

For the flow of a homogeneous liquid through a capillary tube, the expression has been deduced:

$$n = \frac{pr^4t}{8V_1}$$

where p is the driving force, r is the radius of the tube, t is the time required for the volume, V, of liquid to flow through the tube of length 1.

The Determination of Viscosity

1. *Oswald's Method.*—The apparatus usually employed for the determination of the viscosity of liquids in general is the Oswald modification of Poiseuille's apparatus, a careful description of which is given by Dunstan and Strevens (*J.S.C.I.*, 1912, 31, 1063), and by Savill and Cox (*J.S.C.I.*, 1916, 35, 151). Cf. Higgins (*J.S.C.I.*, 1913, 32, 568), Strevens (*J.S.C.I.*, 1914, 33, 109). This consists of a U-tube, one arm of wide tubing about 40 cm. in length having a bulb at the lower end, the other arm consisting in part of a capillary tube of about 0·4 mm. bore at the upper end of which is a bulb having marks placed immediately above and below. In order to make a determination, a definite volume of liquid is introduced into the bulb in the larger limb by means of a pipette, and is then forced up into the narrow limb until the level of the liquid is above the mark placed immediately above the bulb. The liquid is then allowed to flow back into the wider tube, and the time taken by the liquid to flow from the mark above the bulb in the capillary tube to the one below accurately observed. The same observation is then made on some standard liquid such as water when, if n and n_1 be the coefficients of viscosity respectively, s and s_1 the specific gravities, and t and t_1 the times of outflow, then

$$\frac{n_1}{n} = \frac{s_1t_1}{st}.$$

It will be seen that this expression gives the relative viscosity of the second liquid—the coefficient of viscosity in absolute units may be expressed by substituting that for the comparison liquid in the above equation.

This method has obvious disadvantages in the case of oils, where convenience and speed must be taken into serious account. For this reason a number of instruments have been suggested which measure the time taken for a known volume of the liquid to flow through an orifice of known but relatively large dimensions, others such as the Doolittle torsion viscometer

use more indirect methods. Of the efflux type of viscometer, that of Redwood is the best known in this country, where it is the instrument nearly always mentioned in specifications. Other instruments are due to Saybolt, Engler, Barbey, Lamansky and Nobel, etc.; as these are similar in principle to that of Redwood they need not here be described in detail. For a modification of this apparatus cf. G. F. White (*Analyst*, 1912, 37, 143), as also *J.S.C.I.*, 1920, 39, 812A.

2. *The Redwood Viscometer.*—This instrument was designed many years ago by Redwood (*J.S.C.I.*, 1886, 5, 126). It consists essentially of a silvered-copper vessel, fitted at the bottom with an agate jet of standard dimensions, to contain the oil to be tested, the whole being surrounded by a bath, fitted with a stirrer, which can be heated to any desired temperature. The oil vessel has a stopper consisting of a metal sphere attached to a wire, the sphere resting upon a hemispherical cavity in the jet; there is also a small bracket fitted with an upturned point, which serves to indicate the point to which the vessel must be filled with oil. A determination is made in the following way:

After having made sure that the jet is clean and dry (this and the careful treatment of the jet are most important), set up the apparatus and level by means of the adjustment screws. Fill the water-jacket with water and heat to the necessary temperature. Fill the oil vessel with the sample to be tested (it is, of course, of the utmost importance that the oil be free from water and solid impurities), until the level of the liquid just reaches the point supplied. When the oil has attained the exact temperature desired, raise the ball and allow the oil to run into a 50 c.c. graduated flask placed underneath, taking the time necessary to fill the flask by means of a stop-watch.

Redwood recommends that the results obtained be compared with refined rape oil by means of the formula

$$\text{Viscosity} = \frac{n \times 100 \times s}{535 \times 915}$$

where n is the number of seconds recorded and s the specific gravity of the oil, 535 being the average time of efflux in seconds for pure rape oil; as a general rule, however, it is more useful simply to record the actual time of outflow under the standard conditions, careful mention being made of the temperature at which the determination is made.

The conversion of Redwood viscosities into absolute viscosities has been shown by Archbutt and Deeley (*Lubrication and Lubricants*), to be readily possible. The matter has been further examined by Savill and Cox (*J.S.C.I.*, 1916, 35, 151), who find that the connection between viscosity and seconds flow in a Redwood viscometer can be expressed by a straight line graph. The Redwood instrument may be calibrated in the following manner as suggested by Archbutt and Deeley:

Prepare eight solutions of purest glycerin in distilled water as set out in the table on page 488 and take their specific gravities at 20°/20°. Determine the efflux time for each solution, and for pure water in the viscometer at 20°. Ascertain now the density (d) of each solution by multiplying the S.G. 20°/20° by 0·99826 (the density of water at 20°) and find the viscosity from the table (due also to Archbutt and Deeley) of viscosities on page 488. The variation in the viscometer for liquids of different viscosities, usually symbolised as K, is given by

$$K = \frac{n}{td}$$

where t is the time of efflux in seconds, and d is the density. The various values of K for the different solutions are then plotted in the form of a curve, so that all intermediate values of K corresponding to td may be read off.

In order to determine, then, the absolute viscosity by means of the Redwood viscometer, the efflux time is first determined, and then the density of the solution determined by multiplying the specific gravity at 40°/15° by 0·9991 and thus find $t \times d$. Then by means of the curve for the particular viscometer, prepared as described above, read off the value of K (Archbutt and Deeley found that for oils having viscosities below 40 it is more exact to take the value of K corresponding to 7/5 td), which multiplied by td will give the absolute viscosity or

$$n = \mathrm{K}.t.d.$$

The Temperature of Working.—Unfortunately, as yet, there is no standard temperature or temperatures at which viscosities are observed. Results have been published at almost all temperatures from 0° to 150° and higher. These figures are valuable in some instances as showing the variation in viscosity from one temperature to another, but it is highly desirable that some standard temperature should be agreed upon to which all workers would conform. There is much to recommend the 40° suggested by Fryer and Weston, as it is the same temperature at which refractive indices are now usually observed and at this point even fats are molten. It will be, however, desirable to have two other temperatures, one high and one lower, for work of special character; for this temperatures of 20° or 25° and 100° would have much to recommend them.

Further notes on the relation of viscosity to other properties and the viscosity of mixtures are given in the following papers :

Kessler and Mathiason.	*J.S.C.I.*, 1911, 30, 372.
G. F. White.	*J.S.C.I.*, 1912, 31, 442.
White and Thomas.	*J.S.C.I.*, 1913, 32, 32.

The viscosity of some vegetable oils as determined in the Redwood vixcometer by Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 990) are shown in the following table :

TABLE XXIX.—VISCOSITY OF VEGETABLE OILS (CROSSLEY AND LE SUEUR)

Oil.	Efflux Time.* 70° F	Oil.	Efflux Time. 70° F.
Linseed	212	Radish seed	385
Tung	858–1433	Arachis	307–429
Walnut	232	Olive	312
Safflower	247·8–294	Mahua	90–107
Poppy seed	254–259	Phulwara	110·4
Amoora	376	Malabar tallow	101–104
Niger seed	263–293	Kokum butter	101
Argemone	269–272	Coconut	64
Garden cress	322		

* Number of seconds for 50 c.c. of water in the same viscometer at 70° F. = 25·4.

Figures given by Fryer and Weston (*Oils, Fats and Waxes*) are the absolute viscosities multiplied by one hundred.

Liquid.	N × 100.
Water	0·657
Sperm oil	17
Olive oil	34
Rape oil	40
Castor oil	248

The figures given by various instruments with the same oil have been determined by W. Meissner and are given in the following table :

Table XXX.—Viscosities of Vegetable Oil (Meissner)

	At °C.	Seconds for Outflow in Viscosimeters.			
		Engler's. 200 c.c.	Engler's. 200 c.c.	Redwood. 50 c.c.	Saybolt-"Universal." 60 c.c.
Water	20	51·26	51·39	26·47	28·55
Rape oil	50	236·1	237·0	142·5	169·1
Rape oil	20	735·1	736·6	424·5	515·6
Lubricating oil	150	362·3	362·9	221·1	258·6
Lubricating oil	120	2525	2527	1490	1759

Specific Gravity

The various methods for the determination of specific gravity are so well known that it will not be necessary in this place to go into great detail in their description beyond pointing out the various modifications and precautions which are necessary in the examinations of oils and fats.

In the case of fats liquid at the ordinary temperature the determination is usually carried out at 15° or 15·5°, in glass, compared with water at the same temperature. When, as in the case of fats solid at this temperature, another one is used it is usual to express this by employing a fraction the numerator of which gives the temperature at which the determination was made and the denominator that of the standard volume of water. Thus, to state that the specific gravity of an oil is 0·917 15·5°/4° means that its specific gravity at 15·5° is 0·917 compared with an equal volume of water at 4°. The standard temperature usually adopted in this country is 15·5°/15·5°; in America and some tropical countries 25°/25° is more usual. The temperature 15°/15° was fixed at the International Conference on Food Analysis held in Paris in 1910 (*Analyst*, 1911, 36, 538) except for solid fats where a wide choice is suggested—such figures will not differ materially from those obtained at 15·5°/15·5°, so that this standard should be adopted.

Solid Fats.—In taking the specific gravity of fats in the solid condition it is very important to see that the substance is free from air bubbles. The best method of ridding the material of these is to melt the substance and then allow it to cool thoroughly in an evacuated desiccator.

The determination is best carried out by attaching to a piece of suitable

size another solid (say a piece of lead) which is sufficiently heavy to submerge the lighter body in water. The specific gravity is then determined by finding the weight of the substance in air, the apparent weight of the substance and sinker in water (by attaching to the hook of the balance pan by means of a very fine piece of platinum wire and allowing them to hang in a beaker full of water resting on a wooden stirrup standing clear of the balance pan) and the apparent weight of the sinker by itself in water. If w is the weight of the fat in air, w_1 the apparent weight of the fat and sinker in water and s the apparent weight of the sinker in water, then the specific gravity of the fat is given by

$$D = \frac{w}{w - w_1 + s.}$$

The specific gravity of solid fats is frequently taken at a temperature at which they are liquid; the methods used are given below under liquid fats.

Liquid Fats.—The determination of the specific gravity of liquid fats may be carried out roughly by means of a hydrometer, somewhat more accurately, but not quite so readily, by means of the Westphal balance, and with a high degree of accuracy (usually higher than is really necessary) by means of some form of specific gravity bottle or pyknometer. Other rough methods, usefully described as flotation methods, will also be described.

1. *The Hydrometer.*—The ordinary hydrometer is made of glass and consists of a stem carrying a scale on which the specific gravity is read, a cylindrical body, and a lower bulb containing mercury in order to cause the whole to float upright. The liquid to be tested is contained in a small cylinder sufficiently wide to take the hydrometer comfortably. The hydrometer is put in carefully making sure that there are no adherent air bubbles and that the stem is wet with the liquid for a short distance above the level of the liquid. For transparent liquids it is better to take the reading by looking under the surface, having the eye on a level with the surface, and taking the point where this appears to cut the hydrometer as the true reading.

When using the hydrometer in the examination of oils the main difficulty arises (assuming the correctness of the instrument and the fact that it is floating freely without touching the bottom or sides of the containing jar) from the viscosity of the oil which causes some time to elapse before the true position is assumed. To avoid error in this direction it is a good plan to take two readings, one after the hydrometer has been placed a little below the point of equilibrium and allowed to rise and the other when it has been placed a little above and allowed to fall. By selecting suitable instruments the method may be reasonably accurate for routine determinations.

2. *The Westphal Balance.*—This is a balance on the steel-yard principle, at one end of which hangs a plummet which displaces exactly 5 c.c. of water. When the plummet hangs in air the balance is adjusted so that the two points are exactly opposite to one another. When the plummet is immersed in some liquid, riders have to be added to bring the balance again into equilibrium. The largest rider weighs five grams (for a 5 c.c. plummet), so that the first decimal place is shown by the position of this on the beam when the system is in equilibrium, other riders are used being one-tenth, one-hundredth, and one-thousandth of this—these, therefore, show the second, third, and fourth decimal places respectively. For liquids denser than water one of the largest riders is hung from the plummet hook. Should it happen that two riders occupy the same notch on the beam, the smaller is hung from the larger.

The Westphal plummet can be used in connection with an ordinary

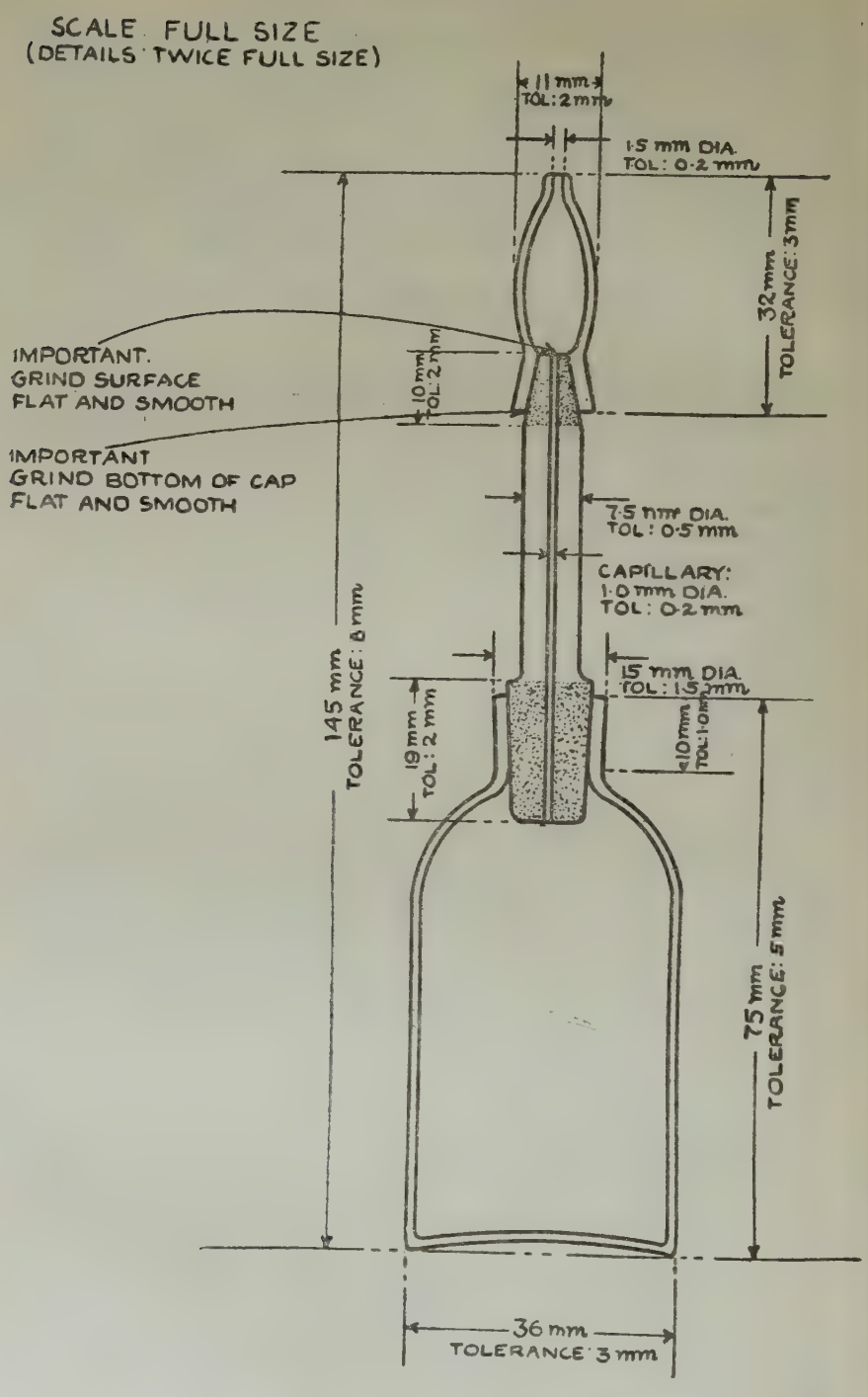
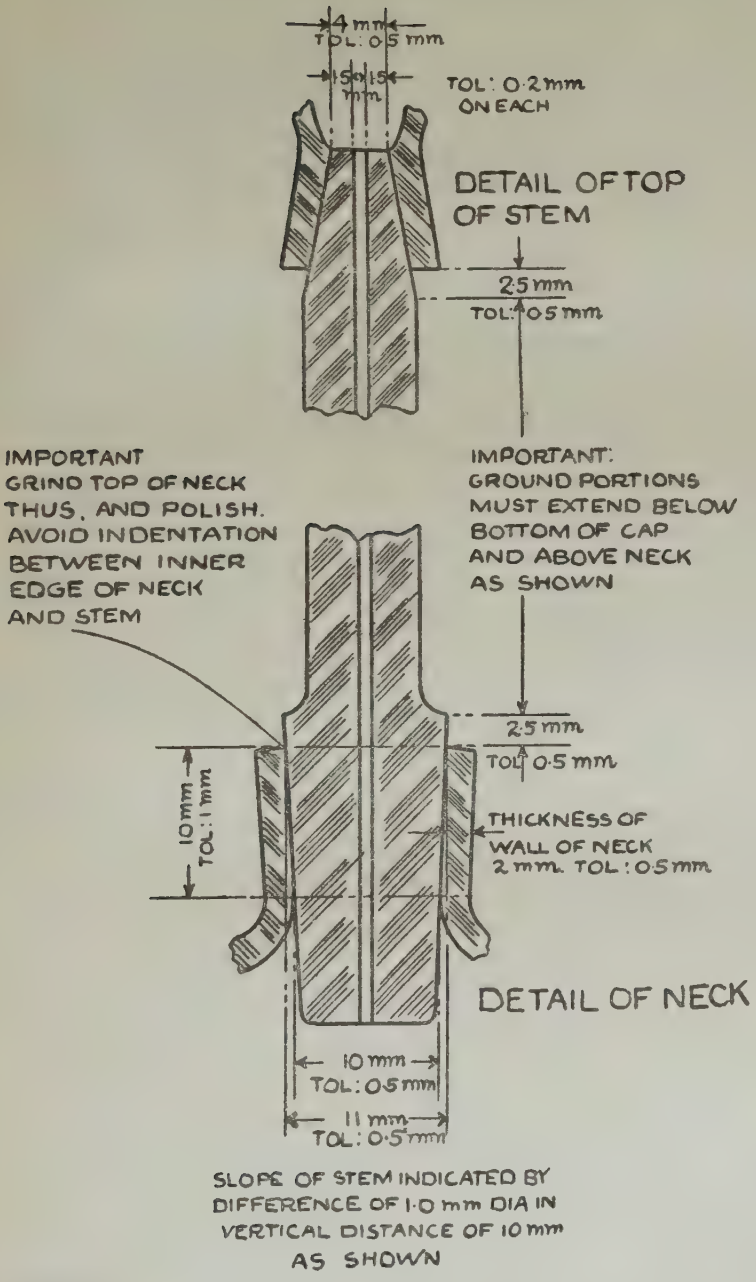


FIG. 2.—

General Description: Pyknometer or specific gravity bottle, consisting of three parts, viz., bottle, cap- Pyrex glass, capillary stem to be made of regular stock, all parts to be thoroughly annealed. *Grinding* : of bottle, and of cap on upper end of capillary stem. *Base:* Bottom slightly concave as shown, to stand engraved on each instrument, the same serial number to appear on each of the three separate parts. in separate box.


4 mm
TOL: 0·5 mm
1·5 mm
1·5 mm
TOL: 0·2 mm ON EACH
DETAIL OF TOP OF STEM
2·5 mm
TOL: 0·5 mm
IMPORTANT GRIND TOP OF NECK THUS, AND POLISH. AVOID INDENTATION BETWEEN INNER EDGE OF NECK AND STEM
IMPORTANT: GROUND PORTIONS MUST EXTEND BELOW BOTTOM OF CAP AND ABOVE NECK AS SHOWN
2·5 mm
TOL 0·5 mm
10 mm TOL: 1 mm
THICKNESS OF WALL OF NECK 2 mm. TOL: 0·5 mm
DETAIL OF NECK
10 mm
TOL: 0·5 mm
11 mm
TOL: 0·5 mm
SLOPE OF STEM INDICATED BY DIFFERENCE OF 1·0 mm DIA IN VERTICAL DISTANCE OF 10 mm AS SHOWN

YKNOMETER

[*By permission of Mr C. A. Mitchell*

ary stem and cap. *Capacity:* 50 ml., tolerance 5 ml. *Material:* Bottle and cap to be made of be done with the utmost care, insuring perfect fitting of stopper portion of capillary stem into neck flat surface. *Special Marking:* Manufacturers' serial number, and name, initials or trade-mark to be *imensions:* To be as shown and within the specified tolerances. *Case:* Each instrument to be packed

balance, which is, in general, more delicate than the Westphal balance. The jar holding the liquid to be tested is placed on a fixed support striding the balance pan and so arranged that the latter can move freely without coming in contact with it. The method is capable of considerable accuracy when plenty of time is allowed for the balance to take up its true position of equilibrium.

3. *The Specific Gravity Bottle.*—There are various types of this bottle, most of which are useful and many of which give results of considerable accuracy. Probably the most accurate form is that which has an internal thermometer and also a capillary side tube having a ground glass cap. This type has been adopted for the determination of the specific gravities of glycerin by the International Committee. The specifications for such a bottle are as below:

Base.—Bottom slightly concave as shown, to stand on flat surface.

Neck.—Should be thoroughly ground with tight joint. Thermometer rigid when in place with no indentation between tip of neck and thermometer.

Thermometer.—Thickness of glass as near as possible to $\frac{1}{6\frac{1}{4}}$th in. Extremities of bulb approximately equidistant from shoulder and base of body to pyknometer. The joint at the lower end of the thermometer should contain no unground portions, and should project slightly above the top of the neck. Scale range from 10° to 40° graduated in $\frac{1}{5}$th°. Accuracy to be guaranteed within 0·2° between 15° and 20°. Scale of opalescent glass to be sealed rigidly in place.

Capillary.—Ground portion fitting into cap to be ground true without shoulder below lower end of cap to prevent ridge forming or wearing.

Numbering.—All instruments to be numbered serially, same number to be shown on bottle, cap and thermometer of each instrument and manufacturer's initials to be etched on bottle.

Capacity.—Approximately 50 c.c.

Note.—Each pyknometer to be packed in separate box.

The method of using this instrument in connection with glycerin as described by the Industrial Committee is given below, liquid oils may be examined in a similar manner:

"The pyknometer used in the sp. gr. estimation on glycerin should be of the standard 50 c.c. Geissler type, provided with a piece of glass tubing 6 cm. in length and attached to the side tube of the pyknometer by means of a piece of rubber tubing 2·5 mm. in diameter and 2 cm. in length. The thermometers should be calibrated at four points, namely, 15°, 20°, 25° and 30°, and each instrument should be furnished with the thermometer corrections for these four temperatures.

Prepare the pyknometer, either for standardisation or for use, by first cleaning the interior with chromate cleaning solution, thoroughly rinsing with water, alcohol and ether, and expelling the ether by a current of air, which has passed through a drying train which will free it from dust, grease, moisture and acid. Under no circumstances subject the pyknometer to any considerable elevation of temperature. Wipe the pyknometer first with a damp cloth and then with a dry cloth or with filter-paper. This standard method for preparing the pyknometer for accurate weighing insures uniformity with respect to the invisible film of moisture present on glass surfaces.

The method of standardising the pyknometer should parallel the procedure indicated for the estimation of glycerin, except that freshly-boiled distilled water, which has been cooled to about the temperature of the constant temperature bath, is substituted for the glycerin. The capacity

in grm. of water at 15·6° is calculated from the weight of water obtained at $t°$, corrected by the following formula:

$$C = W.\frac{D}{d} \cdot \frac{1}{1+a(t-15\cdot6)}$$

in which t = Observed temperature.
W = Capacity in grm. at $t°$.
C = Capacity in grm. at 15·6°.
D = Density of water at 15·6°.
d = Density of water at $t°$.
a = Thermal coefficient of cubical expansion of glass = 0·00025 per 1°.

The procedure actually suggested for filling the bottle with glycerin and weighing is given below:

Place the tubing attachment firmly over the end of the pyknometer capillary, and transfer the glycerin to the pyknometer, avoiding air bubbles. Wipe the lip and inside of the neck of the sample bottle with a clean, dry cloth before and after pouring out the glycerin to prevent getting any diluted glycerin in the pyknometer. Also wipe the stopper of the sample bottle with a dry cloth before replacing it in the bottle. After filling the pyknometer, carefully draw up the glycerin in the tubing attachment until it appears well up in the capillary. Set the thermometer firmly in place and wash the whole apparatus free of the surplus glycerin. Set the pyknometer in a constant temperature water-bath and maintain the temperature of the bath constant until the thermometer in the pyknometer and the thermometer in the bath register the same temperature, and allow to remain for a period of 10 minutes longer to make sure that the temperature of the glycerin is the same throughout the pyknometer. Carefully remove the tubing attachment and wipe the excess glycerin from the top of the capillary with a dry finger before removing the pyknometer from the water. After removing the pyknometer from the water, wipe the ground portion of the capillary quickly with a piece of filter-paper, and replace the cap tightly. Wipe the whole pyknometer, first with a wet cloth, and then with a dry cloth, and weigh rapidly.

Calculation:

$$\frac{G}{C} \cdot \frac{1}{1+a(t-15\cdot6)} + B\,(t-15\cdot6) = \text{Sp. gr. at}\,\frac{15\cdot6°}{15\cdot6°}.$$

in which t = Observed temperature.
G = Grm. glycerin at t.
C = Capacity of pyknometer in grms. of water at 15·6°.
a = Coefficient of expansion of glass = 0·000025 per 1°.
β = Thermal coefficient of expansion of glycerin.
= 0·00061 between 15·6° and 20°.
= 0·000615 between 20° and 25°.
= 0·00062 between 25° and 30°.

Where work of the greatest accuracy is required it is, of course, necessary to take into account the displacement of the air by the pyknometer, and also by the weights. In order to obtain the true weight (*i.e.*, the weight which the body would have in a vacuum) of a body weighed in air with brass weights, we must add to *each gram* apparent weight, G, the quantity $\left(\frac{0\cdot0012}{d} - 0\cdot00014\right)$

grams. The following table, due to Kohlrausch, gives the value of this correction *in milligrams* for different values of *d*, where *d* is the specific gravity for the body being weighed.

TABLE XXXI.—TABLE OF CORRECTION VALUES IN SPECIFIC GRAVITY TESTS (KOHLRAUSCH)

d.	Correction mgs. per grm.	*d.*	Correction mgs. per grm.	*d.*	Correction mgs. per grm.
0·7	1·57	2·0	0·457	9	−0·010
0·8	1·36	2·5	0·337	10	−0·023
0·9	1·19	3·0	0·257	11	−0·034
1·0	1·06	3·5	0·200	12	−0·043
1·1	0·95	4·0	0·157	13	−0·051
1·2	0·86	4·5	0·124	14	−0·057
1·3	0·78	5·0	0·097	15	−0·063
1·4	0·71	5·5	0·075	16	−0·068
1·5	0·66	6·0	0·057	17	−0·072
1·6	0·61	6·5	0·042	18	−0·080
1·7	0·56	7·0	0·029	19	−0·080
1·8	0·52	7·5	0·017	20	−0·083
1·9	0·49	8·0	0·007	21	−0·086

These precautions, although essential where results of the highest numerical accuracy are required, are quite unnecessary in the ordinary examination of oils. In general it will only be necessary to divide the weight of oil by the weight of the equal volume of water, both being at 15°.

The following table, giving the specific gravity of water at various temperatures, will be useful for calculating the volume of the bottle when this is not obtained exactly at 15°.

TABLE XXXII.—SPECIFIC GRAVITY OF WATER AT DIFFERENT TEMPERATURES

Temperature. °C.	Specific Gravity.	Temperature. °C.	Specific Gravity.
9	1·00071	16	0·99985
10	1·00063	17	0·99966
11	1·00053	18	0·99948
12	1·00041	19	0·99928
13	1·00028	20	0·99907
14	1·00015	21	0·99886
15	1·00000		

4. *The Sprengel Tube.*—The Sprengel tube is really a convenient form of specific gravity bottle susceptible of great accuracy and of great value for the determination of specific gravities at temperatures other than that of the room. As it can be made of almost any size by the use of light capillary tubing throughout it is particularly useful where only small quantities of oil are available. It consists essentially of a U-tube the ends of which are drawn out to a capillary and bent at right angles having ground glass caps

to fit. One of the capillary tubes is drawn out to a point and the other has a mark on it. For use the whole is filled with the liquid and immersed in a bath of water at the required temperature. When no further expansion or contraction takes place the liquid is carefully adjusted on the mark by applying a piece of filter-paper to the pointed end; it is then wiped and weighed.

This method is particularly useful for the determination of the specific gravity of solid fats in the liquid state, in fact, it is the only completely satisfactory method. For such purposes the limbs are usually made at an obtuse angle with the body rather more than at right angles, as in this way it is easier to submerge the whole of the liquid in the hot bath at the required temperature. Where observations are carried out at high temperatures, such as 40 or 100, it is not necessary to take the expansion of the glass into account if the volume of water is obtained by weighing the tube filled with this liquid at the same temperature as that at which it is weighed filled with the fat.

5. *Flotation Methods*.—Two flotation methods have been used to a certain extent. The first consists in the use of a number of glass pellets having varying known specific gravities. These are placed in the liquid to be examined; those having a lower specific gravity than the liquid will float, whilst those having a higher will sink. By observation of the respective values it will be possible to obtain a rough idea of the specific gravity of the oil.

The second method is particularly valuable as by its means it is possible to determine with a fair degree of accuracy the specific gravity of a single drop of oil provided that the oil is not soluble in alcohol and that it does not contain an excessive amount of free acids. To carry out the determination a suitable quantity of alcohol (industrial) is placed in a cylindrical tube one drop of the oil added and then water drop by drop until the oil just, and only just, rises to the surface. The specific gravity of the mixture is then determined by some suitable means (the hydrometer or Westphal balance will be sufficiently accurate) which gives the specific gravity of the oil. Bellmer (*Analyst*, 1911, 36. 557) has constructed a table giving the gravity of the solution from the amount of water added.

A few drops of the oil under examination are introduced into 2 c.c. of absolute (98 to 99 per cent.) alcohol, and water added little by little from a burette until the drops just begin to float. The specific gravity may then be found by reference to the following table from the amount of water added :

TABLE XXXIII.—SPECIFIC GRAVITIES BY FLOTATION METHOD (BELLMER)

Water c.c.	Sp. Gr. at 15° C.	Water c.c.	Sp. Gr. at 15° C.	Water c.c.	Sp. Gr. at 15° C.	Water c.c.	Sp. Gr. at 15° C.
0·1	0·8178	1·1	0·9050	2·1	0·9376	3·1	0·9537
0·2	0·8331	1·2	0·9091	2·2	0·9397	3·2	0·9548
0·3	0·8456	1·3	0·9133	2·3	0·9417	3·3	0·9558
0·4	0·8563	1·4	0·9173	2·4	0·9436	3·4	0·9568
0·5	0·8678	1·5	0·9209	2·5	0·9453	3·5	0·9577
0·6	0·8739	1·6	0·9243	2·6	0·9469	3·6	0·9587
0·7	0·8812	1·7	0·9273	2·7	0·9485	3·7	0·9595
0·8	0·8880	1·8	0·9301	2·8	0·9499	3·8	0·9603
0·9	0·8940	1·9	0·9327	2·9	0·9512	3·9	0·9610
1·0	0·8995	2·0	0·9353	3·0	0·9525	4·0	0·9617

The Temperature Correction.—It is not always possible to take the specific gravity of an oil exactly at 15°. In order to overcome this difficulty Allen determined the coefficient of expansion of a large number of oils between the boiling-point of water and various lower temperatures. His figures were obtained by means of the Westphal balance without correction for the expansion of the glass of the plummet, so that they are not absolutely correct—they are, however, sufficiently accurate for small adjustments due to varying temperatures. The correction figures for 1° for seventeen kinds of fat varied between 0·000615 and 0·000665 with a mean figure of 0·00064; this latter figure may be taken as nearly correct and its use will introduce no appreciable error for small differences of temperature. Such factors should not be used where the respective temperatures differ by more than a few degrees except for rough comparisons (cf. Wright, *J.S.C.I.*, 1907, 26, 513; 1916, 35, 457).

The Effect of Free Acids.—Various statements have been made from time to time in regard to the effect of free fatty acids on the specific gravity of an oil. Allen was of the opinion that the figure was lowered to a slight

TABLE XXXIV.—SPECIFIC GRAVITY OF FATS AT 15° C.

Oil.	Sp. Gr.
Rape group	0·913–0·916
Egg	
Bone	
Neat's-foot	0·913–0·920
Sheep's-foot	
Horse's-foot	
Almond	0·916–0·920
Arachis	
Olive	
Horse fat	
Hemp seed	0·920–0·925
Soya bean	
Maize	
Cotton seed	
Sesamé	
Palm oils	
Fish oils	0·920–0·935
Linseed	0·925–0·935
Laurel	
Coconut	
Palm kernel	
Lard	0·935–0·940
Butter fat	
Tallow	0·935–0·950
Tung	
Nutmeg butter	0·940–0·960
Castor oil	0·950–0·960
Croton oil	
Cacao butter	0·950–0·970

extent by the presence of such free acids and although Thomson and Ballantyne (*J.S.C.I.*, 1890, 9, 588) and Lewkowitsch contest this statement it would appear from general principles and from the work of A. O. Ransome (*J.S.C.I.*, 1912, 31, 672) that this is really the case. Ransome found that in the case of olive oil an increase in the acid value of 10° lowered the specific gravity by 0·008.

The Method Recommended.—For routine work with liquid fats the Westphal balance will be found convenient and sufficiently accurate. For more accurate work and for use with solid fats at elevated temperatures the Sprengel tube has advantages which do not obtain to the bottle—its use is, therefore, recommended under these conditions.

CHAPTER IX

CHEMICAL TESTS

Acid and Saponification Values

The methods given below are those adopted by the Committee of Analysts appointed by the Director of Oils and Fats in November 1918.

Acid Value.—Definition.—The acid value of a fat or oil is a measure of the free fatty acids present, and is defined as the number of mgrms. of potassium hydroxide required to neutralise the free fatty acids in 1 grm. of the fat or oil—i.e., parts of potassium hydroxide which are required to neutralise the free fatty acids in 1000 parts of the fat or oil.

Chemicals Required.—(*a*) Alcoholic alkali solution, N/10 and N/2 potassium or sodium hydroxide, accurately standardised. (*b*) Neutral alcohol, 94 to 95 per cent. (by volume), containing 0·2 grm. of phenolphthalein per litre. This may be conveniently prepared by redistilling industrial methylated spirits free from mineral oil over sodium hydroxide, adding the phenolphthalein and subsequently neutralising.

The Test.—The necessary quantity of the fat or oil is carefully weighed into a 250 c.c. flask, and about 50 c.c. of the alcohol are added. The mixture is gently boiled, well shaken to thoroughly dissolve out the free fatty acids, and titrated while still warm, and with constant agitation, with N/10 alkali till the pink colour is permanent on shaking for ten seconds. Towards the end of the titration the alkali should be added drop by drop in order to avoid an excess until the end point is reached.

As a rule, 5 grms. of the sample will be found a suitable quantity, but in the case of refined fats or oils this should be increased to 10 grms. If more than 10 c.c. N/10 alkali solution are required for the test, it should be repeated with N/2 alkali.

Then, if X = number of c.c. of N/10 solution,
F = weight of fat or oil taken,

$$\text{Acid value} = \frac{X \times 5{\cdot}61}{F}.$$

In order to express the acidity in percentages of oleic acid, the following formula should be used:

$$\text{Oleic acid per cent.} = \frac{X \times 2{\cdot}82}{F}.$$

In the case of fats obtained from the kernels of the coconut group, such as coconut oil, palm-kernel oil, tucum, babassu, cohune, etc., the acidity is calculated as lauric acid, when the following formula should be used:

$$\text{Lauric acid per cent.} = \frac{X \times 2{\cdot}0}{F}.$$

Acid value = per cent. oleic acid × 1·99 = per cent. lauric acid × 2·80.

Saponification Value.—Definition.—The saponification value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1000 parts of the fat or oil.

Solutions Required.—(*a*) N/2 hydrochloric acid accurately standardised. (*b*) An alcoholic solution of potassium hydroxide or sodium hydroxide, approximately N/2, prepared by dissolving 18 to 20 grms. of stick potassium hydroxide in not more than 10 c.c. of distilled water, and making up to 500 c.c. with 94 to 95 per cent. (by volume) alcohol. The solution is allowed to stand for twenty-four hours, and the clear liquid siphoned off for use. Potassium hydroxide may be replaced by sodium hydroxide, but this substitution is not desirable. The alcohol must be free from mineral oil and of such a purity as to yield a nearly colourless solution after twenty-four hours. (*c*) An alcoholic solution of phenolphthalein, 1 per cent.

The Test.—About 2 grms. of the clear filtered fat are accurately weighed into a 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol added, and 25 c.c. of the alcoholic potassium hydroxide solution, accurately measured, run in. A like quantity of the same solution is run, in exactly the same way, into a similar flask, together with 25 c.c. of the neutral alcohol. The flasks are connected to reflex condensers and heated, preferably in a water-bath, so that the alcohol boils briskly for thirty minutes. The flask containing the fat should be shaken with a rotary movement from time to time during the period. The contents of the flasks are then titrated while hot with the N/2 acid after the addition of 1 c.c. of the phenolphthalein solution.

If F = grms. of fat taken,
X = c.c. of acid required in the control experiment,
Y = c.c. of acid required to neutralise the excess of alkali in the test,

$$\text{then saponification value} = \frac{X - Y \times 0{\cdot}02805 \times 1000}{F}.$$

N.B.—The saponification equivalent $= \frac{561{,}000}{S}$: this is the number of grms. of fat saponified by 56·1 grms. of KOH or one litre of normal alkali. There is no advantage in the use of this over the saponification value which is retained exclusively in this book.

In order to keep the oil in solution during the titration, a mixture of alcohol and ether has been recommended, but H. Loebell (*J.S.C.I.*, 1911, 30, 409), states that the titration in such a solution, owing to the slight extent of dissociation, is incorrect. He recommends a mixture of 2 parts of benzene to 1 part of 96 per cent. alcohol, the titration being completed with N/10 sodium hydroxide after the addition of 50 c.c. of water to the alcoholic solution. Loebell's method is recommended by Steele and Sward (*J.S.C.I.*, 1922, 41, 260A), particularly for tung oil and for oils having a small acid value. (Cf. H. F. Slack, *J.S.C.I.*, 1915, 34, 1259.)

Kremann and Muss (*J.S.C.I.*, 1921, 40, 896A), as also Kremann and Schopper (*J.S.C.I.*, 1922, 41, 675A), have used conductivity methods as a means of the determination of the acid value. The results obtained are in agreement with those obtained by titration, but the method would not appear to have any particular advantages.

Pennington and Hepburn (*Analyst*, 1910, 35, 248), found that the acid value of the crude fat of fowls (without any separation other than mechanical) gave an indication as to freshness or otherwise.

Acid Value and Saponification Value (*Combination Method*).—The acid value and saponification value may, if so desired, be determined upon the same weight of the sample in the following manner:

About 4 grms. of the clear filtered fat or oil are accurately weighed into the saponification flask, and 25 c.c. of hot alcohol containing 1 c.c. of phenolphthalein solution, and previously neutralised, are added. The free fatty acids are titrated from a burette with the alcoholic alkali solution as used for the saponification value, warming if necessary during the titration. The number of c.c. required by the free fatty acids having been noted, such a further quantity of alcoholic alkali as will make a total of 50 c.c. is added, and the process continued as described above.

A blank test is made with 50 c.c. of the alcoholic alkali delivered from the identical burette, using similar quantities of all the reagents. The exact value of the alcoholic alkali having been determined with N/2 hydrochloric acid, the acid value and saponification value may be respectively calculated.

In carrying out the above processes it is very desirable that the alcohol should produce very little colour when boiled with potash in the absence of the oil. Industrial methylated spirit may be used if it is first boiled under a reflux condenser with 10 per cent. of potassium hydroxide, and then redistilled. Waller (*Analyst*, 1890, 15, 50) suggests that the alcohol is shaken with powdered potassium permanganate until it assumes a distinct colouration. It is then allowed to stand for some hours until the permanganate has been decomposed and hydrated manganese peroxide has settled. A pinch of calcium carbonate is then added, and the alcohol distilled from a flask, provided with an efficient fractionating column. The distillate is tested frequently until 10 c.c., when boiled with 1 c.c. of a strong (syrupy) solution of caustic potash, gives no yellow colouration on standing for twenty or thirty minutes. What distils after that is preserved for use; care, however, must be taken not to distil to dryness.

Carter Bell (*J.S.C.I.*, 1893, 12, 236) uses the following method : 500 c.c. of methylated alcohol, of about 85 or 90 per cent., are placed in a flask of about 1000 c.c. capacity, with 25 grms. of stick potash. When the latter has dissolved, 250 grms. of melted lard (or of some other saponifiable fat) are added. The flask is then connected with an inverted condenser and heated on the water-bath, so as to saponify the fat. Then the condenser is reversed, and about 450 c.c. of alcohol are distilled off.

In the case of oils producing very dark coloured solutions M'Ilhiney (*J.S.C.I.*, 1895, 14, 197) suggested the determination of the alkali used by means of the amount of ammonia it will liberate from an ammonium salt. In general, however, equally good results will be obtained by diluting the dark coloured solutions with strong alcohol. Another method is suggested by R. Pschorr (*J.S.C.I.*, 1921, 40, 593A), whilst the use of mercuric chloride as an indicator is proposed by H. Pomeranz (*J.S.C.I.*, 1919, 38, 588A).

In place of ethyl alcohol higher alcohols have been suggested, as on account of the higher boiling-points of these the time of saponification is reduced (this is particularly convenient in the case of waxes) and the use of a reflux condenser is rendered unnecessary. L. W. Winkler (*J.S.C.I.*, 1911, 30, 556) proposes the use of propyl alcohol, and Pardee, Hasche and Reid (*Analyst*, 1920, 45, 268) normal butyl alcohol.

In the table below are given saponification values of the simple triglycerides.

TABLE XXXV.—SAPONIFICATION VALUES OF TRIGLYCERIDES (LEWKOWITSCH)

Triglyceride.	Formula.	Molecular Weight.	Saponification Value.
Simple triglycerides—			
Acetin	$C_3H_5(O{\cdot}C_2H_3O)_3$	218	772·0
Butyrin	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	557·3
Valerin	$C_3H_5(O{\cdot}C_5H_9O)_3$	344	489·2
Caproin	$C_3H_5(O{\cdot}C_6H_{11}O)_3$	386	436·1
Caprylin	$C_3H_5(O{\cdot}C_8H_{15}O)_3$	470	358·1
Caprin	$C_3H_5(O{\cdot}C_{10}H_{19}O)_3$	554	303·7
Laurin	$C_3H_5(O{\cdot}C_{12}H_{23}O)_3$	638	263·8
Myristin	$C_3H_5(O{\cdot}C_{14}H_{27}O)_3$	722	233·1
Palmitin	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	208·8
Hydnocarpin	$C_3H_5(O{\cdot}C_{16}H_{27}O)_3$	794	211·9
Stearin	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	189·1
Olein	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	190·4
Linolin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Chaulmoogrin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Linolenin	$C_3H_5(O{\cdot}C_{18}H_{29}O)_3$	872	193·0
Clupanodonin	$C_3H_5(O{\cdot}C_{18}H_{27}O)_3$	866	194·3
Ricinolein	$C_3H_5(O{\cdot}C_{18}H_{33}O_2)_3$	932	180·6
Arachin	$C_3H_5(O{\cdot}C_{29}H_{39}O)_3$	974	172·7
Erucin	$C_3H_5(O{\cdot}C_{22}H_{41}O)_3$	1052	160·0
Cerotin	$C_3H_5(O{\cdot}C_{26}H_{51}O)_3$	1226	137·3
Melissin	$C_3H_5(O{\cdot}C_{30}H_{59}O)_3$	1394	120·7
Hydroxystearin	$C_3H_5(O{\cdot}C_{18}H_{35}O_2)_3$	938	179·4
Dihydroxystearin	$C_3H_5(O{\cdot}C_{18}\ HO_{35}O_3)_3$	986	170·7
Trihydroxystearin	$C_3H_5(O{\cdot}C_{18}H_{35}O_4)_3$	1034	162·8
Sativin	$C_3H_5(O{\cdot}C_{18}H_{35}O_5)_3$	1082	155·0
Linusin	$C_3H_5(O{\cdot}C_{18}H_{35}O_7)_3$	1178	142·2

The saponification value of the natural fats lies for the most part between 180 and 200, the exceptions to this are placed in the table below—the values for the other fats will be found under their respective headings.

TABLE XXXVI.—SAPONIFICATION VALUES OF A GROUP OF NATURAL FATS

Oil or Group.	Sapon. Value.	Oil or Group.	Sapon. Value.
Stillingia	210	Paradise nut	174
Henbane	171	Birch seed	211
Para-rubber seed	206	Oleander	203
Service berry	208	Fish oils	150–212 *
Hawthorn seed	173	Chaulmoogra group	207–213
Spindle-tree	230	Nux vomica	170
Rape-oil group	170–180	Inukusu	241
Owala	168	Macassar	222
Elderberry	209	Mafura tallow	200–220
Ucuhuba	220	Ochoco	239
[5] Dika group	235–280	Coconut group	240-260
Butter	220–235	Japan-wax	217–238
Myrtle-wax	209	Attaba	256·6
[2] Areca nut	227–234	[9] Elm-tree	277
[5] Virola guatemalensis	244	[6] Acrocomia cilerocarpa	254
[7] Myristica platysperma	240	[1] Akebi seed	247
[7] Coyal palm	246	[3] Aburachan seed	274
[4] Curua palm	260	[8] Lindera obstiroba	264

[1] *J.S.C.I.*, 1916, 35, 1091.
[2] *Analyst*, 1909, 34, 64.
[3] *J.S.C.I.*, 1916, 35, 1092.
[4] *Analyst*, 1921, 46, 50.
[5] *Analyst*, 1910, 35, 536.
[6] *Analyst*, 1914, 39, 134.
[7] *J.S.C.I.*, 1915, 34, 499, 1061.
[8] *J.S.C.I.*, 1921, 40, 856A.
[9] *Analyst*, 1912, 37, 201.

DETERMINATION OF UNSAPONIFIABLE MATTER

The term " unsaponifiable matter " as used in the examination of fats refers to those substances which are not hydrolysed by caustic alkali, are soluble in ether and insoluble in water. As a general rule the amount of such substances occurring in natural fats is small, the usual quantities being of the order of 1 per cent. In the case of vegetable and terrestrial animal oils the unsaponifiable matter consists largely of higher monohydric alcohols (cf. sterols, page 40) which have characteristic properties. Various other substances including resins, colouring matter and hydrocarbons are present in varying small amounts. In certain cases, such as some fish oils, the amount of hydrocarbons may become considerable.

The nature of the alcohols present may lead to valuable methods of identifying an oil. The matter has been discussed at some length by Marcusson and Meyerheim (*J.S.C.I.*, 1914, 33, 491), the following is an abstract of the paper:

" Various natural fats, including tallow, whale oil, and vegetable oils, contained from 0·03 to 0·38 of cholesterol or phytosterol (determined by the digitonin method), the highest proportion being found in linseed oil and the lowest in tallow. The phytosterol constituted from 33 to 55 per cent. of the unsaponifiable matter of the vegetable oils, and the cholesterol from

* Due to varying proportion of unsaponifiable matter.

8 to 14 per cent. of the unsaponifiable matter of the animal fats. The other constituents consisted in the main of dextrorotatory alcohols which neutralised, wholly or in part, the optical lævorotation of the cholesterol or phytosterol. For example, the sesamin in sesamé oil caused the unsaponifiable matter to have $[\alpha]_D = +52°$. This characteristic may be used as a test for sesamé oil in cases where the colour reactions give negative results through previous treatment of the oil. The unsaponifiable matter, after removal of the cholesterol or phytosterol as digitonides, was a thick oily substance, containing dextrorotatory alcohols, with the exception of that from tallow which contained lævorotatory alcohols. Only in the case of dark marine animal oils (*Tranen*) were there more than traces of hydrocarbons. The unsaponifiable matter of sesamé oil freed from cholesterol showed $[\alpha]_D = +102°$. The iodine value of the unprecipitated unsaponifiable matter of the fats examined ranged from 56 to 78, or about the same as that of the cholesterol or phytosterol (68). Small quantities of hydrocarbons may be detected by this test. As a rule hydrogenated fats contained less cholesterol or phytosterol than the original fats, the proportion decreasing with the degree of hardening. The other constituents of the unsaponifiable matter were yellow and semi-solid. From ' talgol ' and ' candelite ' a saturated alcohol was extracted with petroleum spirit. It melted at 59·3° to 59·8° and had the refraction at 100° of octodecyl alcohol (1·4268). On hydrogenation cholesterol was resinified to the extent of about 75 per cent. at 200°, whilst phytosterol was not appreciably affected. At 250° cholesterol no longer yielded crystalline derivatives, though these could still be obtained from phytosterol. This explains why cholesterol cannot be precipitated with digitonin from ' talgol,' and similar products from animal fats."

The Determination.—The actual determination may be carried out by evaporating the alcohol from the solution of the fat which has been used for the saponification value, dissolving the soap in water and extracting the resulting soap several times with ether. The mixed ethereal solutions are washed with a little water to remove dissolved soap and then evaporated to dryness and the residue weighed.

This process, so simple in outline, is yet so difficult in practice on account of the very troublesome emulsions which are produced on the slightest provocation. For this reason many modifications and improvements have been suggested, some of which are given below.

Revis and Bolton's Method.—Five grms. of the fat are weighed into a large porcelain basin and heated with sufficient strong aqueous solution of caustic soda to introduce 2 grms. of NaOH and 100 c.c. of strong (95 per cent.) alcohol, the dish being covered with an inverted funnel. The dish is heated on a boiling water-bath with occasional stirring for thirty minutes, after which the contents are evaporated to a pasty condition, when a teaspoonful of sand and 2 to 3 grms. of sodium bicarbonate are added, and the whole carefully mixed and carried to dryness. The contents of the dish are then well ground, thoroughly dried, and carefully transferred to a flow-through extractor, and extracted for two or three hours with petroleum ether. The contents of the extractor are dried, removed to a mortar, again thoroughly ground, dried in the water-bath and extracted as before for another hour. The contents of the flask are then evaporated, dried and weighed as unsaponifiable matter.

Wilkie's Method.—J. M. Wilkie (*Analyst*, 1917, 42, 200) has modified the wet extraction method in the following way; troublesome emulsions are largely avoided by using such a ratio of the volumes of alcohol and ether :

Weigh 5 grms. of the oil into a flask, add 12·5 c.c. 2N alcoholic potash,

heat for about one hour and a half, transfer to a separator with 50 c.c. of water, extract with 40, 30, 30 c.c. ether, unite the ether extracts in a separator containing about 20 c.c. of water. Without shaking, run off completely the wash water, and wash the ethereal solution by shaking vigorously with 2, 5 and 30 c.c. water; evaporate and weigh the residue.

In the ordinary way separation is as rapid as when ether and water are shaken together, though in cold weather it may be more sluggish; but, if the soap solution after drawing off from the first and second extractions is heated on the water-bath until the dissolved ether obviously commences to distil, no trouble is experienced. In very warm weather it is sometimes an advantage to allow the separation to take place under reduced pressure by placing in running water for a few minutes.

In the case of waxes Wilkie uses a somewhat different method which is as follows:

Saponify 0·5 grm. of the beeswax (truly representative of the bulk) and 4·5 grms. of castor oil with 12·5 c.c. 2N alcoholic potash for one hour, complete precisely as the ether method (already described), but use 40 c.c. water at 30° instead of 50 c.c. cold water, and extract with 50, 40, 40, 30 c.c. ether. Wash with 2, 5, 30 c.c. water, evaporate and weigh. Apply a correction for the known unsaponifiable content of the castor oil. Other solid waxes and lanolin (wool wax) may be treated precisely as beeswax.

In Wilkie's paper he gives a number of determinations of unsaponifiable matter which he made; these are reproduced in the following table:

TABLE XXXVII.—UNSAPONIFIABLE MATTER IN OILS AND FATS (WILKIE)

	Percentage of Unsaponifiable Matter.	Number of Samples.
Castor oil	10·4 to 0·7	3
Cod-liver oil, medicinal	0·8 „ 1·4	100
Lard	0·2 „ 0·4	3
Linseed oil	1·0 „ 1·5	13
Neat's-foot oil	0·5 „ 1·2	23
Olive oil	0·7 „ 1·5	62
Palm oil	0·5	1
Poppy-seed oil	0·4 to 0·6	3
Rape (Colza) oil	0·8 „ 1·4	32
Whale oil	0·8 „ 1·4	12
Waxes—		
Sperm oil	34·3 to 43·6	22
Spermaceti	51·0 „ 52·5	2
Beeswax, yellow	52·3 „ 55·5	10
„ white	50·0 „ 54·4	13
Lanolin (wool wax)	41·0 „ 51·8	19

J. B. Rather (*Analyst*, 1915, 40, 159), acidifies the saponified solution and extracts fatty acids and unsaponifiable matter, together with ether. The ethereal solution is extracted several times with a solution of sodium hydroxide, and finally the ethereal solution is evaporated and the unsaponifiable matter weighed. E. Twitchell (*J.S.C.I.*, 1915, 34, 433),

treats the unsaponifiable matter as extracted with alcohol and titrates the alcoholic solution with standard acid. The acids so found are calculated as oleic acid and subtracted from the gross weight to give the true weight of unsaponifiable matter. Where the soap solutions themselves are extracted Lewkowitsch recommends that the unsaponifiable matter be ignited, the ash treated with water, filtered and the filtrate titrated with decinormal acid. The alkali found is calculated to soap and this figure deducted from the gross weight of the unsaponifiable matter. A modified method for the determination of unsaponifiable matter is made by W. Fahrion (*J.S.C.I.*, 1920, 39, 697A).

Kerr and Sorber (*J.S.C.I.*, 1925, 44, B16), use the following method:

Five grms. of fat in 15 c.c. of boiling 95 per cent. alcohol are saponified by adding another 15 c.c. of boiling alcohol containing 3 c.c. of potassium hydroxide solution (100 g. in 100 c.c. of water), and boiling the mixture for a few minutes. The solution is then cooled, mixed with 50 c.c. of ether, transferred to a separating funnel, and the flask washed with two 50 c.c. portions of ether. After adding 150 c.c. of distilled water and rotating the mixture in the funnel, the soap solution is drawn off, the ether solution washed with water until free from alkali, transferred to a weighed vessel, the ether evaporated, and the residue dried and weighed.

The Sterol and Sterol Acetate Tests

On account of the fact that the sterols contained in animal and vegetable oils are not identical, and also that in general animal oils contain only cholesterol whilst vegetable fats contain chiefly sitosterol, the examination of the sterol of a given fat is a valuable aid to a decision as to whether it contains animal or vegetable fats only, or a mixture of the two. Many writers have described the sterol acetate test as final and conclusive, but the work of Steuart (*Analyst*, 1923, 48, 158), which has already been mentioned several times, throws a certain amount of doubt on the subject, in fact, Steuart says that, although " an examination of the sterol prepared from a sample of the fat will show definitely whether the fat is of purely animal origin or whether vegetable fat is present " yet " the sterol acetates prepared from some vegetable oils contain fractions of lower melting-point which makes it impossible to detect the presence of animal fats in mixtures containing such vegetable fats by an examination of the sterol acetates." In spite of this, however, the test must still be looked upon as valuable, even on its weaker side, but it must always be interpreted in the light of Steuart's criticisms.

Preparation of the Unsaponifiable Matter.—The first operation in the investigation of the sterols is the extraction of the unsaponifiable matter which may be done on quantitative lines by the method given on page 121, using 50 or 100 grms. of the oil. The extracted material is dissolved in ether and the solution poured into a small glass or porcelain dish suitable for crystallisation. The ethereal solution is allowed to evaporate, the residue is dried on the water-bath, cooled, dissolved in the smallest possible quantity of absolute alcohol and allowed to crystallise.

The form of the crystals so obtained, as seen by microscopic examination, will give some idea as to their composition as cholesterol appears as plates rhombic in form, whilst phytosterols give needles in star-shaped groups. Diagrammatic representations of these crystals are given in the figure. Mixtures of the two kinds of crystals may show the two forms side by side, but in other cases the results given with mixtures are inconclusive.

In cases where crystallisation is difficult or where the presence of colour-

ing matter masks the appearance of the crystals, the solution may be cleared by means of animal charcoal in the usual way. Cholesterol has M.Pt. about 148°, whilst phytosterol melts as a rule at temperatures considerably lower than this. Neither the melting-point nor the microscopic appearance, however, is of any great weight as compared with the phytosteryl acetate test, which is the only one which is used now to any serious extent.

The Phytosteryl Acetate Test.—The phytosteryl acetate test was first introduced by Bömer, who gave the matter lengthy consideration, and whose conclusions have been verified by various workers. The original method has, however, been modified in various ways, chiefly with a view to economy in material.

In the original process Bömer saponified 100 grms. of fat, diluted the soap solution with water and extracted with 500, 250 and 250 c.c. of ether. To obviated the use of so much ether, Von Raumer evaporated the soap solution to dryness, powdered the residue, and extracted with ether in a Soxhlet apparatus. Kreis and Wolff, on account of the difficulty of completely drying the soap, proposed a method based on the extraction of the calcium salts of the fatty acids with alcohol and subsequent extraction with ether, but later this method was found to be unreliable, and Kreis and Rudin devised the following method: 50 grms. of the fat are saponified with 125 c.c. of 95 per cent. alcohol and 25 c.c. of 40 per cent. sodium hydroxide solution, the alcohol evaporated, and the soap dissolved in 50 c.c. of boiling water and precipitated with 100 to 200 c.c. of a 10 per cent. solution of calcium chloride. When cold, the liquid is filtered through a cotton cloth and the calcium soap dried between filter-paper, finely powdered, and allowed to stand in contact with 100 c.c. of a mixture of equal parts of alcohol and ether for one hour with frequent agitation. It is then washed on a filter with 100 c.c. of a mixture of equal parts of alcohol and ether and the filtrate and washings, after evaporation of the ether, mixed with 3 c.c. of a 40 per cent. solution of sodium hydroxide and evaporated to dryness. The residue is mixed with about 20 grms. of quartz sand and dried on the water-bath and subsequently, for one hour, in the hot water-oven. Finally it is extracted with ether in a Soxhlet apparatus, the ethereal extract evaporated, and the residue recrystallised from alcohol.

In many cases, however, the use of somewhat large quantities of solvent will not be considered a serious deterrent, as they may be recovered—simple extraction of the soap solution with ether may then be used. The residue from the first ethereal extractions usually contains traces of unsaponified fat, which is removed by a second saponification with a small quantity of alcoholic alkali, when the solution is diluted with water and extracted with ether. The mixed ethereal extracts are washed two or three times with water, filtered into a flask and the solvent evaporated.

The residue is treated with 2–3 c.c. of acetic anhydride (when the residue has been crystallised for microscopic examination the crystals are returned to the mother liquor, which is then evaporated to dryness) in a small dish covered with a watch glass on the water-bath until the solution boils, after the boiling has continued for a few minutes the acetic anhydride is evaporated off on the water-bath. The residue is dissolved in boiling absolute alcohol (10 c.c. of alcohol for each 0·1 grm. of unsaponifiable matter), a little extra alcohol added to prevent immediate crystallisation and the clear solution (filtered if necessary) allowed to stand at the ordinary temperature. When about half the liquid has evaporated the crystals are filtered through a small filter-paper, washed with two portions of 2 c.c. of cold alcohol, returned to

the crystallising dish and again crystallised from 10 c.c. of absolute alcohol, this process of crystallisation being continued as many times as the material will allow.

The melting-point of the crystals is determined after each crystallisation, beginning with the third. Bömer considers that the presence of a vegetable oil is proved if the temperature of complete fusion is 117° (corr.) or higher.

This process has been examined by various workers who have suggested modifications. These have been reviewed at some length by Hepburn (*J.S.C.I.*, 1913, 32, 989), but since the introduction of the digitonin method (q.v.) the older methods have to a certain extent gone out of use. Cf. *J.S.C.I.*, 1909, 28, 1100; 1901, 20, 1147; 1902, 21, 643; 1912, 31, 239, 826.

The addition of small quantities of paraffin wax has been attempted in order to make the phytosteryl acetate test worthless or unreliable. Much work has been done on this subject by Polenske, whose results have been confirmed by Lewkowitsch. The presence of paraffin lowers the melting-point of the crystals, which may fall considerably below 100°.

The removal of the paraffin wax from the crude unsaponifiable matter is carried out, according to Polenske, by treating the unsaponifiable matter from 100 grms. of fat with 1 c.c. of petroleum ether (boiling below 50°) for twenty minutes at 15°–16°, transferring the mass to a small funnel closed with cotton-wool, and washing with five successive portions each of 0·5 c.c. of petroleum ether. Lewkowitsch adds that the drawback of this method is that a certain amount of the alcohols is washed away with the petroleum ether, but it offers the countervailing advantage that more cholesterol is removed than phytosterol, so that the indications of the phytosteryl acetate test become more distinct, the proportion of phytosterol (if present) to cholesterol being increased.

Polenske determines the proportion of paraffin wax by treating the unsaponifiable matter from 100 grms. of fat with 5 c.c. of conc. sulphuric acid at 104° for one hour, when the alcohols are destroyed and the paraffin remains behind and may be extracted with petroleum ether and weighed. The same process may be used with the petroleum ether extract of the original unsaponifiable matter. Paraffin wax in quantities greater than mere traces will show up after boiling with acetic anhydride, when it will float as a globule (of large or small size depending on the amount present) on the surface of the liquid.

The Digitonin Method.—A reaction common to all sterols is the precipitate given by an alcoholic solution with an alcoholic solution of digitonin. The preparation of digitonin has been described by Panzer (*Chem. Zentral.*, 1912 (ii), 540). It can be obtained commercially, but the price is high and supplies are not always to be obtained. For this reason the method is, as yet, by no means universally used. The reaction was apparently first used by Windhaus (*Analyst*, 1910, 35, 256), for the determination of sterols in biological products. The cholesterol and digitonin combine together to form a precipitate of digitonin cholesteride $C_{55}H_{94}O_{28}\cdot C_{27}H_{46}O$, which is said to be a simple molecular compound of the two substances. The compound is insoluble in water, acetone and ether, and nearly insoluble in 95 per cent. alcohol (the solubility is 0·014 at 18°). The compound is formed by free cholesterol only, and not by its esters.

A certain amount of controversy has arisen over the necessity of saponifying the oil before the addition of the digitonin. Thus Marcusson and Schilling (*Analyst*, 1913, 38, 458), recommended merely shaking a dilute

alcoholic solution of digitonin with the oil, and state that saponification is not necessary, and the same method is adopted by Fritzsche (*Analyst*, 1914, 39, 84). Klostermann, however (*Analyst*, 1914, 39, 32, 310; *J.S.C.I.*, 1913, 32, 1118), states that the method of Marcusson and Schilling is not universally applicable because, as has been stated above, digitonin precipitates only the free sterols and not their esters. Klostermann recommends that 100 grms. of the fat be saponified with alcoholic alkali, the soap solution diluted with water, the fatty acids liberated by means of hydrochloric acid and dissolved in 250 c.c. of ether. The ethereal solution of the fatty acid is separated, washed with water, and shaken with 250 c.c. of petroleum spirit and 25 grms. of sodium chloride, and filtered through cotton-wool. The filtrate is warmed and treated with a solution of 1 grm. of digitonin in 20 c.c. of 90 per cent. alcohol, and the crystalline precipitate separated after fifteen minutes and washed with ether until free from fat. The precipitate is dried with filter-paper and acetylated with 20–30 c.c. of acetic anhydride. The excess of acetic anhydride is evaporated, the residue dissolved in 50 c.c. of absolute alcohol, and the solution treated drop by drop with water until crystals begin to separate. The amount of water added is then increased to 25 c.c., the crystals filtered on cotton-wool, washed with 70 per cent. alcohol, and dissolved in ether. The solution is evaporated to dryness and the acetates are recrystallised from alcohol in the usual way. In a later paper, however (*Analyst*, 1914, 39, 310), Klostermann states that saponification is not necessary in the case of animal fats as these are free from sterol esters, but that in the case of animal oils and vegetable oils most of the sterols occur in the form of esters, and that, therefore, saponification is necessary in their case (cf. Berg and Angerhausen, *J.S.C.I.*, 1914, 33, 1062).

Pfeffer (*Analyst*, 1916, 41, 317) suggests that the digitonin solution be added directly to the fatty acids and the hot mixture poured on to a filter which is placed in the water-oven until the fatty acids have passed through. Chloroform should not be added, as its presence retards the rate of filtration by destroying the granular state of the precipitate. The precipitate and filter are then washed with hot chloroform, next with ether, and the filter dried. The precipitate can then be removed from the filter and treated in the usual way. Lifschutz (*J.C.S.*, 1918, 114, ii, 179) gives a modified method for recovery of the sterol from its digitonin compound which includes a method for recovery of the digitonin. "About 0·5 grm. of the anhydrous complex is weighed out and boiled with 5 c.c. of acetic anhydride for twenty to thirty minutes under a reflux condenser. The hot liquid is poured into about 80 c.c. of water. After the product of the reaction has solidified, it is collected, washed, and dried in a vacuum. It is now removed as completely as possible from the filter-paper, transferred to a small flask, dissolved in 10 c.c. of 90 per cent. alcohol, and mixed with 10 c.c. of 1 per cent. aqueous sodium hydroxide. The resulting emulsion is boiled for two and a half to three minutes, cooled, diluted with water, acidified, and extracted with ether. The cholesteryl acetate dissolves in ether, whilst the digitonin remains in the dilute alcohol. After evaporation of the ether, the cholesteryl acetate is hydrolysed with alcoholic potassium hydroxide, and the free cholesterol or similar compound extracted by ether, weighed, and subsequently identified in the usual way."

Olig (*Analyst*, 1916, 41, 317) considers that, as a general rule, saponification is not necessary and that it is only when an inconclusive result is obtained, which, he states, is seldom, that it is necessary to saponify the fat and make the precipitation from the fatty acids. Various other papers giving

similar or diverse conclusions will be found under the following references :

Kerr	*J.S.C.I.*, 1913, 32, 917.
Barthel and Sonden.	*Analyst*, 1914, 39, 254.
Kühn and Werwerinke	*J.S.C.I.*, 1915, 34, 669.
Kühn, Bengen and Werwerinke.	*J.S.C.I.*, 1916, 35, 126.
Klostermann and Opitz.	*J.S.C.I.*, 1916, 35, 1070.
Dubosg.	*J.S.C.I.*, 1917, 36, 464.
Muttelet.	*J.S.C.I.*, 1922, 41, 65A, 191A.
Gardner and Williams.	*Analyst*, 1921, 46, 508.

Steuart (*Analyst*, 1923, 48, 155) in his work on the sterols of edible fats used the following process: "The unsaponifiable matter from 50 grms. of fat was warmed with 50 c.c. of 95 per cent. alcohol and mixed with 50 c.c. of hot 90 per cent. alcohol containing 0·5 to 1 grm. of digitonin. After standing overnight the precipitate of digitonin steride was filtered off, washed on the filter-paper with 95 per cent. alcohol and with ether and weighed after drying at 110° C. Per cent. of sterol $=(\text{Wt.}+0{\cdot}014)\times 0{\cdot}243\times 2$. The steride was then transferred to a small beaker and about 1 c.c. of acetic anhydride added per 0.1 grm. of steride, the beaker covered with a watch glass, and the liquid boiled until the steride had dissolved. On cooling, nearly all the sterol acetate crystallised out (Olig, *Zeitsch. Nahr. Genussm*, 1914, 28, 129). This was filtered off and the crystals dried with the aid of suction, dissolved through the filter-paper with ether and, after the ether had evaporated, dissolved in absolute alcohol. As the crystals of acetate separated out they were filtered off, and another or several crops thus taken from the alcohol. The wet crystals, thrown on a porous plate, were kept overnight at 37° C. before the melting-points were determined. In some cases on boiling the acetic anhydride mother liquid down to half the previous volume and cooling, another crop of crystals was obtained. This was worked up as before and the melting-point taken" (cf. *J.O.A.C.*, 1915, 1, 513).

It has been found that hydrogenation of an oil reduces considerably the amount of sterol present. Marcusson and Meyerheim (*J.S.C.I.*, 1916, 35, 549) found the amount of sterol to be reduced from 0·13 to 0·02 by hydrogenation of marine animal oil.

The Process Recommended.—It cannot be said that a really final method for dealing with the sterols of fats on which an exact interpretation can be founded has yet been evolved; further work is urgently needed. In the present state of our knowledge probably the most convenient and satisfactory method is the use of digitonin on the fatty acids along the lines suggested by Klostermann, whose process is given in full on page 126.

In those cases where digitonin cannot be obtained or where the expensive nature of the compound makes its use prohibitive, the phytosteryl acetate test, carried out on the unsaponifiable matter extracted in the usual way, will be found fairly reliable even if somewhat laborious (cf. *J.S.C.I.*, 1924, 43, B964; *Analyst*, 1924, 49, 537, 543).

Separation of the Sterols.—Windaus (*Analyst*, 1906, 31, 411) has suggested a method for the separation of cholesterol from phytosterol by a process which depends upon the insolubility of cholesterol dibromide in a mixture of glacial acetic acid and ether—phytosterol dibromide being much more readily soluble. The bromine is added as a 5 per cent. solution in glacial acetic acid. The dibromides, it is stated, can be readily reconverted into the original alcohols by treatment with zinc dust, sodium amalgam or other similar reducing agent. Holde states that the method is unreliable where

only small quantities of cholesterol are present, but Lewkowitsch states that it is quite suitable when the amount of animal fat amounts to 20 per cent. of the mixture. When smaller amounts of animal fat are present Lewkowitsch suggests a preliminary partial separation by means of petroleum ether, in which cholesterol is much more soluble than phytosterol. For the hydrolysis of cholesterol dibromide see Lifschütz, *J.S.C.I.*, 1919, 38, 922A.

The method of Windaus is carried out by Bolton and Revis (*Fatty Foods*, page 50) in the following way :

> " The sample is treated as usual, preferably in lots of 200 grm., and the alcoholic extracts united. The final dry mixture of soaps, sand and unsaponifiable matter is extracted most simply by heating it in a flask under a reflux condenser with sufficient petroleum ether to rather more than cover the solid matter. After boiling gently for one hour the ether is filtered off and the solid matter dried and reground and boiled twice more with petroleum ether. The combined ethereal extracts are then distilled to obtain the unsaponifiable matter. This is carefully shaken with a very small quantity of petroleum ether, increasing the amount until about one-quarter of the total remains undissolved (cholesterol is more soluble than phytosterol). The ether solution is filtered and distilled off, and the residue is treated by the method of Windaus (*Chem. Zeit.*, 1906, xxx, p. 1011). To each gramme of the residue are added 10 c.c. of dry methylated ether and solution effected. To the solution are added 10 c.c. of a solution of 5 grm. of bromine (dry) in 100 c.c. of *glacial* acetic acid and the mixture cooled in ice for an hour. If only small quantities of cholesterol are present the dibromide will not separate, in which case 50 per cent. acetic acid is added until a permanent turbidity appears. A further 2 to 3 c.c. of the 50 per cent. acetic acid are then added, and after a short time the precipitate filtered off on a very small hard filter and washed with a few drops of the 50 per cent. acetic acid. The filter-paper and contents are dropped into a small flask, 5 c.c. of glacial acetic acid and about 0·25 to 0·5 grm. of zinc dust added, and the whole boiled under a reflux condenser for two hours. The contents of the flask are then washed into a *small* separator with 20 c.c. of water and finally with 10–20 c.c. of methylated ether and the whole shaken. The aqueous layer is run off and the ether washed three times with a little water and filtered (if necessary) into a test-tube and the ether boiled off. The residue is dried in the water-oven and then washed out with a very small quantity of absolute alcohol into a small evaporating basin and evaporated to dryness. The residue is covered with 1–2 c.c. of acetic anhydride, and the basin closed with a clock glass and heated on a water-bath for thirty minutes. The acetic anhydride is then distilled off, and the residue, if much coloured, washed with absolute alcohol into a test-tube and boiled with a little recently ignited powdered animal charcoal. The mixture is filtered (washing the charcoal with a little absolute alcohol) into a small beaker, evaporated to dryness and recrystallised from the least possible quantity of 95 per cent. alcohol; the crystals are separated, recrystallised from 95 per cent. alcohol, and the melting-point taken, and further crystallisations carried out if possible. The crystals, if cholesteryl acetate, should melt below 116° C. Twenty per cent. of cholesterol in the presence of phytosterol can be found by this means, and probably 10 per cent. may be found with care when a large quantity of material is employed to start with."

The Insoluble Bromide Value

When oils containing glycerides of unsaturated fatty acids are treated with bromine in ethereal solution, bromine is absorbed, and the bromine addition compounds of the unsaturated acids are produced. It is obvious that oleic acid will produce dibromides, whilst the more highly unsaturated acids may produce tetrabromides, hexabromides and, in the case of the highly unsaturated acids of fish oils, octobromides. In general the dibromides and the tetrabromides are moderately soluble in ether, whilst the hexabromides and octobromides are almost insoluble in this solvent as, indeed, they are in most organic solvents, particularly in the cold. When carried out on the mixed fatty acids of an oil, the only insoluble compound which will be formed (in the absence of fish oils) will be linolenic hexabromide, or its isomerides, so that the weight of precipitate obtained would be a measure of the linolenic acid present, but when the original oil is brominated the insoluble compounds produced are probably from mixed glycerides. Thus Toms (*Analyst*, 1924, 49, 77) has deduced evidence of the preparation in this way from linseed oil of linolic dilinolenic bromo-glyceride $C_{57}H_{94}O_6Br_{16}$.

It was early considered that this reaction might be of value in the examination of oils, and in 1898 Hehner and Mitchell (*Analyst*, 1898, 23, 310), continuing the investigations made by Hazura some ten years earlier suggested the following process, using the oil and not the fatty acids:

Hehner and Mitchell's Process.—From 1 to 2 grms. of the glycerides are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid are added, the precipitate forming being more granular from such a mixture than when ether alone is employed. The solution is cooled in an ice-chest and bromine added, the flask being preferably left all night in the ice. This, however, is not essential for ordinary working. The liquid is filtered off by the suction funnel attached to a pump, the flask washed out with four successive portions of 10 c.c. of ether at 0° C., and the residue dried in the flask to constant weight. But even when ether at ordinary temperature is used no considerable error is introduced.

Sprinkmeyer and Diedrichs (*Analyst*, 1912, 37, 403) give the following results for various oils found by using this method. Linseed oil, 28·9; candlenut oil, 8·8; hempseed oil, 8·82; walnut oil, 2·22; soya-bean oil, 3·62; sesamé oil, 0·14; mustard oil, 1·30; rape oil, 1·92 per cent. Poppy-seed oil, sunflower-seed oil, maize oil, cotton-seed oil, castor oil, tea oil, earthnut oil, coconut oil, palm oil, palm-kernel oil, cacao butter, stillingia tallow, tulucana fat, dika fat, and malukang butter, did not yield an insoluble bromine compound. In the case of shea butter, different specimens of the fat yielded from 5·2 to 8·6 per cent. of bromine compound, whilst mowrah butter gave 0·82 per cent., enkabang tallow, 0·17 per cent. and adjab fat 2·2 per cent. As regards the four last-mentioned fats, the bromine compound appears to be formed from the unsaponifiable matters present, the fatty acids derived from the fats yielding no bromine compound after they have been freed from unsaponifiable matter.

Lewkowitsch worked at a temperature of 5°, used a fluted filter, and operated on the fatty acids rather than on the oil itself. Procter (*J.S.C.I.*, 1906, 25, 798) used carbon tetrachloride as the solvent, worked on the oil itself and precipitated the bromides by the addition of absolute alcohol. Bull and Johannesen (*Analyst*, 1909, 34, 110) prefer to use the fatty acids. They stated that they had had trouble during the filtration as proposed by Hehner and Mitchell, and to avoid this, they cool to 0° for the precipitation and filter through a Soxhlet filter tube after standing for three hours at the

ordinary temperature; they state that duplicate determinations usually agreed within 0·5 per cent. Ingle (*J.S.C.I.*, 1911, 30, 344) worked on the oil at ordinary temperatures and found results considerably higher than those of Hehner and Mitchell.

Marcusson and Huber (Seifensieder, *Zeit.*, 1911, 38, 249) suggest a modification, a negative result in which Stiepel (*Analyst*, 1913, 38, 35) considers to be inconclusive evidence of the absence of marine animal oils.

Eibner and Muggenthaler (*Analyst*, 1913, 38, 158) state that " the utility of the test depends upon the determination of the linolenic acid, the constituent of most importance in the drying process, which acid gives a hexabromide insoluble in cold ether, whilst the simultaneously formed tetrabromide of isolinolenic acid is dissolved." These workers have devised an elaborate test, based on a long series of experiments, in which the solutions are cooled to −10°, and work on the fatty acids. Their method does not appear to give such improved results as to make worth while the use of such an inconvenient temperature as −10°.

Sutcliffe (*Analyst*, 1914, 39, 28, 388) reinvestigated the process and was able to suggest a rapid method of working which was convenient for general laboratory use and which is probably the best method (taking all things into consideration) so far suggested. It is described in detail below on page 131. Gemmell (*ibid.*, 1914, 39, 297), in a lengthy paper considers it far better to work on the fatty acids, but the results obtained do not appear to warrant the additional trouble involved (cf. Revis and Bolton, *Analyst*, 1915, 40, 502).

Steele and Washburn (*Analyst*, 1920, 45, 101) operate on the fatty acids and use chloroform containing 3 per cent. of alcohol as the solvent, cool to −5°, evaporate the solvent under diminished pressure and wash the residue with ether saturated with hexabromide at 0°. The washings are carried out in a centrifuge tube in which the washed bromides are weighed after drying at 60°–70°. Concordant results are reported, but these do not support the statement of the authors that " the hexabromide yield obtained in this way is a more constant value than is the iodine value of linseed oil," because eight linseed oils having iodine values of 181–185 (a divergence of 2·2 per cent.) gave yields of hexabromide which ranged from 45·6–46·9 (a divergence of 2·8 per cent.). Wolff (*J.S.C.I.*, 1920, 39, 417A) combines the determination of the insoluble bromide value with that of the unsaponifiable matter. This method is a contrifugal one, using ether at temperatures below 0° as the solvent, and is preferred by Wolff to that of Steele and Washburn, because the yields are somewhat higher and give better differentiation between oils of different iodine value. A similar process has been suggested by Bailey and Baldsiefen (*Analyst*, 1921, 46, 104), but it has been stated (*J.S.C.I.*, 1920, 39, 604A) that the results are somewhat lower and less concordant than those given by Steele and Washburn's method. It is further criticised by Eibner (*J.S.C.I.*, 1921, 40, 355A), who compares it unfavourably with his own method and with that of Steele and Washburn. He states that the presence of fish oils as adulterants of linseed oil may be detected by testing the solubility of the octobromides in boiling benzol, and the determination of the M.Pt. of the solute. Davidson (*Analyst*, 1921, 46, 466) considers it desirable to apply the test to the oil, and not to the fatty acids—he uses a very similar method to that of Steele and Washburn.

The problem has been attacked in quite a different manner by H. Toms (*Analyst*, 1924, 49, 77), who has shown that the precipitate obtained by brominating linseed oil is a mixture of two substances, one of which is more soluble than the other. This work at once opens up several new fields of investigation and suggests lines along which a really standard process might be evolved.

Sutcliffe's Method.—This seems to be the best method yet available, and can be recommended as occupying little time and giving reasonably concordant results. One grm. of oil is taken in a tared flask and dissolved in 40 c.c. of redistilled ether, 5 c.c. of glacial acetic acid are added, and the flask and contents cooled to about 11° C. in water. Bromine is added drop by drop with constant shaking till an excess is denoted by the red colour of the solution and the flask is corked and allowed to stand overnight in water. The contents of the flask are filtered through a Gooch crucible prepared in the ordinary way, with a small circle of filter-paper fitted over the asbestos. This enables the bromides to be separated for the melting-point determination. The precipitate is kept as much as possible in the flask during the first three washings with 10 c.c. quantities of cooled ether, and is then transferred to the Gooch crucible for the two final washings. (Before filtration the flask and contents are cooled to below 5° C., and the red ether solution is decanted through the filter. The bromides are washed with cooled ether, and whilst settling, the filter-paper is washed free from bromine with an ether jet.) The Gooch crucible and flask are dried for three hours in the water-oven, and are weighed. After weighing, the melting-point of the bromides is determined. In the case of linseed oil, this should be from 141° to 144° C.

Quantitative Drying Tests

It has already been pointed out in an earlier chapter that the drying oils, and the semi-drying oils to a lesser extent, have the power of absorbing oxygen from the atmosphere and forming an insoluble skin which makes the oils of value for paints, varnishes and the like. It is obvious that the drying power, which is practically equivalent to its capacity for absorbing oxygen, is one of the most important of the determinations which it is desirable to make when examining an oil of this class. In addition to the qualitative drying test which is described under linseed oil on page 174 and which is capable of giving very useful results in experienced hands, many efforts have been made to devise a test which will give quantitative results for the drying power of oils.

The earlier investigators, and, indeed, some of the later ones also, exposed the oil itself to the action of the atmosphere in various ways and observed the gain in weight of the oil so treated. Weger, for example, carried out a long series of experiments with a method of this kind and his results are quoted at length by Lewkowitsch (Vol. I, page 475), but the method is not suitable for use as an ordinary laboratory method.

On account of the length of time required for a simple drying experiment of this kind various suggestions have been made for the addition of " driers " to the oil before exposure. Livache (*J.S.C.I.*, 1886, 5, 494) used a precipitated metallic lead powder on which the oil is dropped (0·6 grm. of oil to 1–2 grms. of lead powder), whilst others have used precipitated copper powder. Bishop (*J.S.C.I.*, 1896, 15, 475) spread the oil on precipitated silica and added a little manganese resinate, whilst Krumbhaar (*Analyst*, 1914, 39, 92) has suggested the use of cobalt resinate. Fahrion (*J.S.C.I.*, 1894, 13, 405) impregnated a strip of chamois leather with the oil thus exposing a very large surface to the oxidising power of the atmosphere. Walker (*Bulletin No.* 109, *Bureau of Chemistry, U.S. Dept. of Agriculture*; *Chemical News*, 1910, 102, 57) used powdered litharge, but his method was found to give wildly fluctuating results by Liverseege and Elsdon (*J.S.C.I.*, 1912, 31, 207), who, however, found that, by making the conditions of the test definite, useful results could be obtained with the minimum expenditure of labour in a reasonably short time. This test is described in full below. Fryer

and Weston (*Technical Handbook of Oils, Fats and Waxes*, Vol. II, page 103) use a piece of fine copper gauze of about 160 mesh, which is weighed, dipped in the oil to be tested, allowed to drain, placed on a watch glass and weighed at once and then each day until the maximum weight is recorded. Wilson and Heaven (*J.S.C.I.*, 1912, 31, 565) have suggested a method in which the actual volume of oxygen absorbed is measured. The results obtained in this way would not seem to warrant its use as a routine laboratory method although they are of distinct interest from the theoretical standpoint.

It will probably be found that the simplest of the quantitative tests so far suggested is that by Liverseege and Elsdon, described below, in which the maximum gain in weight of a linseed oil is usually complete in two days and in which little trouble is involved.

A somewhat different method has been suggested by Elsdon and Hawley (*Analyst*, 1913, 38, 3), who extract with ether the residue obtained by drying the oil at an elevated temperature and weighing the extracted matter. Under the conditions of experiment used pure linseed oils give extracts varying from 14·0 to 19·0 the extract varying proportionately to the iodine value according to the following equation where I is the iodine value :

$$\text{Maximum permissible extract} = 81{\cdot}9 - 0{\cdot}35\ \text{I}.$$

Non-drying oils and semi-drying oils give an extract of 100, i.e., they show no drying power at all. The test is carried out as follows :

Two and a half grms. of the oil are weighed into a small dish and transferred by means of a wash bottle containing ether to a 25 c.c. graduated flask. The solution is then diluted to the mark with more ether and the whole thoroughly mixed. 5 c.c. of this solution are then transferred by means of a carefully dried pipette to an Adam's coil (the fat-free strips made for the determination of fat in milk) care being taken that the solution is uniformly distributed over the whole paper. The coils are allowed to dry in the air overnight and then placed on their edge in the steam oven (it is convenient to fold them twice or three times before doing this), so arranged that the whole of the surface is exposed, and allowed to remain for two hours. At the end of this time the coils are removed, rolled up, placed in a Soxhlet fat-extraction apparatus and extracted with ether (S.G. 0·720) for three hours. At the end of this time the ether is evaporated, a little absolute alcohol added, and the flask dried in the steam oven for two hours : it is then cooled and weighed. The following results have been obtained by this method :

TABLE XXXVIII.—RESULTS OF QUANTITATIVE DRYING TESTS (ELSDON AND HAWLEY)

Oil.	Iodine Value.	Livache (Modified) L. and E.	Extract per cent. 2 hrs.
Linseed	192	..	14·0
"	174	13·3	19·2
"	194	17·4	14·0
"	179	14·6	19·0
"	183	15·5	17·4
"	188	16·3	15·2
"	183	15·3	17·6
"	180	15·2	18·6
"	176	13·8	18·8
"	181	15·2	18·0
Colza	99	..	100·6

*Routine Determination of Oxygen Absorbed.**—Litharge is finely powdered and passed through a No. 40 sieve, it is then spread out in a thin layer in an incubator at 20°–22° C. and left overnight in order to gain constancy in weight. About 10 grms. are placed in a German silver dish 3 inches in diameter and 1 inch deep with a flat bottom and parallel sides. The whole is weighed and about 0·7 to 0·9 grm. of oil added. After weighing, 5 c.c. of methylated ether (sp. gr. 0·720) are then added and the litharge spread out in a uniform layer by thoroughly rocking the dish, which is then put into the incubator and weighed after one, two, or more days, until the weight is either constant or diminishing. The gain is expressed as a percentage of the weight of the oil taken. The added ether is almost completely volatilised in half an hour, and tests proved that the amount of residue left by it does not exceed 3 milligrams and is often less.

Proceeding in this way a genuine raw linseed oil ceases to gain in two days, and after that time usually loses. In one case the gain in two days was 17·4 per cent., in three days 16·9 per cent., and in fourteen days 15·9 per cent. In the case of a boiled oil the oxidation is usually complete in one day : one sample gained 14·1 per cent. in one day, whilst after two days the gain was only 13·6 per cent.

Duplicate experiments with an oil have always agreed well; the following successive determinations obtained with a sample of genuine linseed oil, are typical of the degree of accuracy attainable.

Percentage gain, 17·2, 16·8, 17·4, 17·0, 17·4.

Of the other vegetable oils examined, soy showed the largest gain, 8·4 per cent. to 8·9 per cent. being obtained. Cotton-seed oil came next with a gain of 6·6 per cent. The oxidation was usually complete in two days. Colza oil and arachis oil each gained 2·5 per cent., and two samples of olive oil gained 0·6 per cent. and 1·4 per cent. respectively in two days. These samples continued to gain up to twenty-one days, the figures then being 5·7 per cent., 4·1 per cent., 2·5 per cent., and 3·4 per cent. respectively. Of the fish oils whale oil gained 6·4 per cent. and seal 4·9 per cent. in two days. Resin oil behaved peculiarly : it *lost* 0·3 per cent. in one day and then gained rapidly, the figures being 9·9 per cent. in two days, and 19·4 per cent. in thirteen days.

It has been found that in the case of oils of the same kind, a very close relationship exists between the oxygen absorbed and the iodine value (Wijs). In the following tables the oils are arranged in the order of their iodine values; it will be noticed that in nearly every case a fall in iodine value is accompanied by a fall of oxygen absorbed.

Raw Linseed Oil

Iodine value . .	194	188	184	181	180	180	179	176
Percentage gain .	17·4	16·3	15·5	15·1	15·2	15·0	14·6	13·8

Boiled Linseed Oil

Iodine value . .	176	171	168	164	163
Percentage gain .	13·9	13·6	14·1	13·5	12·6

As might be expected the above relationship does not hold strictly when oils of different classes are compared; however, even among such various

* Liverseege and Elsdon (*loc. cit.*).

oils as linseed, rape, cotton-seed, and olive, the same kind of gradation is present.

The following papers may be referred to by those interested in the oxidation of oils:

"The Detection of Blown Oils Mixed with Mineral Oils." Marcusson, *Analyst*, 1906, 31, 51; *J.S.C.I.*, 1911, 30, 292.

Redman, Weith and Brock. "The Drying Rate of Raw Paint Oils." *Analyst*, 1913, 38, 468.

Fahrion. "The Estimation of Rosin in Blown Oils." *Analyst*, 1913, 38, 469.

Hyland and Lloyd. "The Study of Progressive Oxidation in Oils." *J.S.C.I.*, 1915, 34, 62.

Morrell. "The Study of Polymerisation in Linseed and Tung Oils." *J.S.C.I.*, 1915, 34, 105.

Mackey and Ingle. "The Oxidation of Oils in the Presence of Metallic Catalysts." *J.S.C.I.*, 1917, 36, 317.

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The Acetyl Value

When hydroxy acids are heated with acetic anhydride the former become acetylated, the acetyl group going in to the acid molecule at the expense of the hydroxyl group. The amount of acetic anhydride absorbed, which may be determined as the acetyl value, then becomes a measure of the hydroxy acids present although, as Lewkowitsch has pointed out (*Analyst*, 1899, 24, 319), the acetyl value may also indicate free alcohols, oxidised acids, mono and diglycerides and rancidity. The acetyl value may be defined as the number of milligrams of potassium hydroxide required for the neutralisation of the acetic acid obtained on saponifying 1 grm. of the acetylated fat.

The determination was first proposed by Benedikt, but the method now in use is due to Lewkowitsch (*J.S.C.I.*, 1897, 16, 503; *Oils, Fats and Waxes*, Vol. I) and is thus described by this author:

"10 grms. or any other convenient quantity, are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 c.c. to 600 c.c. of boiling water and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely-drawn-out tube reaching nearly to the bottom of the beaker; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed; this is ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes

slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through dry filter-paper in a drying oven to remove water.

The whole operation may be carried out quantitatively, and in that case the fatty matter is washed on the filter with boiling water, until the filtrate no longer reddens sensitive litmus paper. It is advantageous to weigh the fatty matter left on the filter after drying in an oven if it is desired to ascertain preliminarily whether in an unknown fat a notable amount of glycerides of hydroxy acids are present.

About 5 grms. of the acetylated product are then saponified by boiling with alcoholic potash, as is done in the determination of the " Saponification Value." If the " distillation process " be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the filtration process be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage onwards the determination is carried out either by (*a*) the distillation process, or (*b*) the filtration process.

(*a*) *Distillation Process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the potash used, and distil the liquid in a current of steam. 600–700 c.c. of water are distilled off. As a rule this will be quite sufficient, for the last 100 c.c. will be found to require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillate with decinormal potash, using phenolphthalein as an indicator, multiply the number of c.c. by 5·61, and divide by the weight of substance taken. This gives the acetyl value.

(*b*) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid, exactly corresponding to the amount of alcoholic potash employed, and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value is being determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results; the latter requires less time and will, therefore, be found more convenient.

The distilled water used in determining the " value " by either the distillation or filtration process must be carefully freed from carbonic acid by previous boiling, as otherwise serious errors will follow. Even the water used for generating steam in the distillation process should be brought into violent ebullition before the steam is passed into the distilling flask. In the case of very hard water this source of error may easily creep in. Check experiments with pure acetic acid will readily guide the operator. In order to facilitate the separation of the insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount, which need not exceed 1 c.c. of normal acid, must be measured accurately and deducted from the alkali required for determining the dissolved acids.

Lewkowitsch draws particular attention to the fact that his definition of the acetyl value refers to the acetylated oil which is weighed out, and to which the value is calculated.

In the case of fats containing volatile acids the figure obtained for the acetyl value will include these acids. In such cases, therefore, the amount

of alkali required for the volatile acids is separately determined and subtracted from the apparent acetyl value to give the true acetyl value.

The only oil having a high value is castor oil, for which the value is about 150; the figures for other fats vary from 2·5 to 30, whilst carnauba wax gives a figure of about 55.

T. Zerewitinoff (*Analyst* 1914, 39, 41) has suggested the use of the Grignard reagent (magnesium methyl iodide) for the purpose of the determination of the acetyl value, whilst E. B. Elsbach (*J.S.C.I.*, 1924, 43, B23) uses acetyl chloride in a stream of carbon dioxide and notes the increase in weight of the fat before and after acetylation.

E. B. Holland (*Analyst*, 1914, 39, 362) suggests that, in order to be comparable with other results, the acetyl value should be given as the number of milligrams of potassium hydroxide required to saponify the acetyl group taken up by 1 grm. of the fat on acetylation; he suggests the following process:

" Five grms. of the fat are heated with 10 c.c. of acetic anhydride in a boiling water-bath beneath a reflux condenser for one to one and a half hours, after which sufficient ceresin is added to give a solid disc when cold. Prior to cooling, 150 c.c. of boiling water are introduced, and the flask heated on the water-bath with occasional shaking to expel occluded acetic acid. The solid cake left on cooling is heated with a further 150 c.c. of boiling water, this process being repeated about six times until the filtrate is nearly neutral. The solid disc and particles on the filter are then boiled with 50 c.c. of standard alcoholic potassium hydroxide solution and 50 c.c. of alcohol beneath a reflux condenser (with glass beads to prevent bumping), and the excess of alkali titrated with N/2 hydrochloric acid, with alkali blue as indicator. The difference between the saponification value before and after acetylation is the acetyl value."

This method is used by E. André * (*Analyst*. 1921, 46, 251) and supported and slightly modified by L. W. Cook (*J.S.C.I.*, 1922, 41, 299A, by J. R. Powell, *J.S.C.I.*, 1923, 42, 1185A), and also by A. Leys (*J.S.C.I.*, 1922, 41, 148A).

L. Carcano (*J.S.C.I.*, 1919, 38, 687A) states that, as might be expected, the repeated washing of acetylated oils with boiling water causes slight hydrolysis and that the free acidity should be titrated in the cold before the determination of the saponification value of the acetylated product.

A. Grün (*Analyst*, 1920, 45, 105) has pointed out that the formation of inner anhydrides and inner esters may be a serious source of error. He obviates this by preparing the ethyl esters by alcoholysis (page 51), and carrying out the determination of the acetyl value on these.

The Formyl Value of Simmons.—W. H. Simmons (*Analyst*, 1915, 40, 491) has developed a method for the examination of essential oils somewhat analogous to the acetyl value, but depending upon the use of formic acid. Bolton and Revis (*Analyst*, 1915, 40, 500) consider that this process may yield valuable results in the examination of fats, the method being likely to give information similar to the acetyl value in a more expeditious manner. It seems desirable that work should be carried out along these lines.

Halogen Absorption Values

The halogen (absorption) value of an oil is an indication of the amount of halogen which can be absorbed by an oil under certain more or less arbitrary experimental conditions; the value is usually expressed in grms. of halogen

* For a modification suggested by André, see *J.S.C.I.*, 1925, 44, B290.

absorbed by 100 grms. of oil. The values in common use are the Iodine Value and the Bromine Value, of which the former is by far the most important; they are dealt with separately below.

1. The Iodine Value

The first serious work on the quantitative absorption by fats was done by Hübl (*J.S.C.I.*, 1884, 3, 641), who showed that, although the reaction was very slow at ordinary temperatures and irregular at high temperatures, when the iodine was present in alcoholic solution in the presence of mercuric chloride the absorption of iodine took place at a reasonably rapid rate and that concordant results could be obtained. The method is described below. The mechanism of the reaction has been dealt with at length by B. M. Margosches and his co-workers (*J.S.C.I.*, 1924, 43, B341, B564, B719, B877; 1925, 44, B928).

The Hübl Method.—Weigh out a suitable quantity of the fat (vi.) in a small crucible, transfer to a perfectly dry 350 c.c. stoppered flask or bottle and dissolve in 10 c.c. of pure carbon tetrachloride. Then add 25 c.c. of the special iodine solution (a 6 per cent. solution of mercuric chloride in *absolute* alcohol mixed with an equal volume of a 5 per cent. solution of iodine in *absolute* alcohol) and allow to stand overnight *in the dark*. In one or two flasks use only carbon tetrachloride and iodine solution; these serve as blanks. After standing add 15 c.c. of 15 per cent. solution of potassium iodide to each of the flasks and then 150 c.c. of water to each of the flasks with oils and 100 c.c. to the blanks. Then titrate with standard solution of sodium thiosulphate to starch. It is convenient to use a solution of sodium thiosulphate containing 13·72 grms. per litre as in this case each cubic centimetre is equivalent to 7 milligrams of iodine; using this solution the percentage of iodine absorbed is given by

$$\frac{(\text{c.c. thio. used for blank} - \text{c.c. added to oil}) \times 0{\cdot}007 \times 100}{\text{wt. of oil used.}}.$$

It is most important that there should be present *at least* 30 per cent. of iodine in excess. In order to ensure this the quantity of oil to be used in grms. may be obtained by dividing the highest probable iodine value into 40, thus

$$\text{grams of oil to be used} = \frac{40}{\text{highest per cent. of iodine probable}}.$$

Several suggestions for the modification of this test have been proposed. They have been examined by Margosches and Hinner (*J.S.C.I.*, 1924, 43, 640B), who find that the activation of alcoholic iodine solutions depends on the interaction of mercuric chloride and iodine to form iodine monochloride. Cadmium chloride behaves similarly. In using the solution of iodine in acetic acid containing mercuric acetate suggested by Leys (*J.*, 1907, 26, 436) the mercuric acetate is converted into mercuric iodide by the hydrogen iodide produced by the action of iodine on the fat, and the action of the mercury salt is in this case simply that of removing the hydrogen iodide which would otherwise prevent the iodine addition proceeding to completion. The mercuric iodide in Gill and Adam's solution of iodine in methyl alcohol (*J. Amer. Chem. Soc.*, 1900, 22, 12) probably has a similar action.

Various suggestions have been made for leaving out the mercuric chloride and even for working in aqueous solution. B. M. Margosches and his co-

workers (*J.S.C.I.*, 1924, 43, 639B) report good results with a few minutes absorption by dissolving the oil in excess of alcohol, if necessary by heating, adding an N/5 alcoholic solution of iodine and then water, the amount of iodine being back titrated with thiosulphate without the addition of potassium iodide. These workers consider that the presence of potassium iodide inhibits the addition of hypoiodous acid, which is a necessary part of the reaction (*J.S.C.I.*, 1924, 43, 680B).

The Hübl solution has been modified by Waller (*Analyst*, 1895, 20, 280), who makes the solution much stronger than the former and adds in addition 50 grms. of concentrated hydrochloric per litre of solution. This solution gives results which usually agree fairly closely with those obtained by the Hübl method but is not as reliable—it is not used in this country (cf. Ingle, *J.S.C.I.*, 1902, 21, 587). Mergen and Winogradoff (*Analyst*, 1914, 39, 311) state that Waller's solution is much more stable than Hübl's. They also consider that there should be slight excess of iodine over chlorine to prevent substitution. Auguet suggests that the occasional low results given by the Hübl method may be prevented by the addition of a little hydriodic acid (*J.S.C.I.*, 1912, 31, 1137).

L. W. Winkler (*Analyst*, 1925, 50, 523) claims that the use of a 0·3 per cent. bromine solution in glacial acetic acid containing 1 per cent. each of mercuric chloride and crystallised sodium acetate will allow of a determination of the " Iodine value " in less than ten minutes (cf. Bromine Value, page 143). The preparation of the bromine acetic acid solution is given by the same author (*J.S.C.I.*, 1925, 44, B813).

The Wijs Method.—From the theoretical consideration of the chemical changes involved in the Hübl method it was assumed (page 137) that iodine monochloride was the active agent (Wijs, *J.S.C.I.*, 1898, 17, 698; *Analyst*, 1900, 25, 33). Wijs proposed that this substance should be used dissolved in glacial acetic acid. The following method is that recommended by the Committee of Analysts appointed by the Director of Oils and Fats in November 1918.

Iodine Value—Reagents Required—(*a*) *Iodine Solution.*—This is conveniently prepared by dissolving 7·5 grms. of iodine trichloride in acetic acid (minimum strength, 95 per cent.) and solution may be hastened by warming on a steam bath. When dissolved, add to the solution 8·2 grms. of resublimed iodine, assist solution by heating as before, and make up to 1000 c.c. with acetic acid (95 per cent.). The solution is standardised by means of a blank test carried out at the time that it is used, which should be at least twenty-four hours after it is made up. If the solution is heated for a short time by immersion in boiling water, it may be used immediately after cooling.

The quantities of iodine and iodine trichloride here given are not correct. Both H. Dubovitz (*J.S.C.I.*, 1915, 34, 305) and Radcliffe and Polychronis (*J.S.C.I.*, 1916, 35, 340) state that they should be 7·8 grms. of iodine trichloride and 8·5 grms. of iodine. These figures will give 16·3 grms. per litre of iodine monochloride a N/5 solution of which should contain 16·238 grms. per litre. The actual weights are 7·777 grms. of iodine trichloride and 8·461 grms. of iodine.

(*b*) *Sodium Thiosulphate Solution.*—Dissolve 24·8 grms. of the pure salt in 1 litre of distilled water. It is advisable to add 0·5 grm. per litre of sodium bicarbonate to the solution as a preservative. This solution must be standardised by titrating it against pure dry resublimed iodine, but where this is inconvenient the iodine may be liberated from potassium iodide by a known amount of potassium dichromate in the presence of hydrochloric

acid. As the oxidising value of potassium dichromate does not always correspond accurately with that of an equivalent amount of iodine, the potassium dichromate to be used as described below shall first be set against pure dry iodine. The titration is carried out as follows : Weight 0·20 grm. of pure recrystallised $K_2Cr_2O_7$ into a 200 c.c. stoppered bottle, dissolve in 25 c.c. distilled water, add 20 c.c. 10 per cent. potassium iodide solution and 10 c.c. HCl, moisten the stopper with the KI solution, and allow to stand five minutes. Wash down the stopper with distilled water, dilute to about 100 c.c. volume, and titrate the liberated iodine with the sodium thiosulphate solution, using starch solution as indicator. A blank test, using the potassium iodide solution and hydrochloric acid alone, should be carried out, and the necessary deduction, if any, made from the previous titration.

$$0{\cdot}2 \text{ grm. } K_2Cr_2O_7 = 0{\cdot}51768 \text{ iodine}$$

(*c*) *Potassium Iodide Solution.*—A 10 per cent. solution of the pure salt in distilled water.

(*d*) *Solvent.*—Chloroform or carbon tetrachloride to be used as a solvent for the oil. A blank test on the solvent must not show an absorption of iodine equal to more than 0·2 c.c. of the thiosulphate solution.

(*e*) *Starch Solution.*—Use a 1 per cent. solution of soluble starch.

Method.—0·15 to 1 grm. of the sample is weighed into a wide-necked stoppered bottle of about 200 c.c. capacity; 0·15 grm. of a strongly drying oil and a proportionately larger amount for oils or fats of lower iodine value, up to approximately 1 grm. for such fats as coconut and the like. Dissolve the weighed quantity of fat or oil in 10 c.c. of the solvent (*d*) and add 25 c.c. of iodine solution, moisten the stopper with potassium iodide solution, and allow to stand for one hour. In the case of fats having a very high iodine value like linseed, allow to stand for three hours.

After standing, wash the stopper and neck of the bottle down with 15 c.c. of the 10 per cent. potassium iodide solution, mix, and add 100 c.c. of distilled water, and titrate the excess of iodine with the sodium thiosulphate solution. Towards the end of the titration add about 2 c.c. of the starch solution, and shake vigorously after each addition of the thiosulphate solution until the centents of the bottle are colourless.

A blank test, using 10 c.c. of fat solvent and 25 c.c. of the iodine solution must be done with each set of estimations, or at least once daily.

The result is expressed as per cent. of iodine reacting with the fat.

The great advantages of the Wijs method over that of Hübl are that the time required for the completion of the reaction is very much less in the former than in the latter, whilst the solution is more stable. The disadvantages are the properties of the acid solvent which are liability to solidify, possible chemical action due to the acidity and large coefficient of expansion and viscosity requiring great care in pipetting to use identically the same temperature and method for the blanks as well as for the oil itself.

Alternative methods of preparing the solution in addition to that mentioned above are the use of iodine monochloride itself, which can now readily be obtained, and the preparation of the reagent by dissolving 13 grms. of iodine in a litre of glacial acetic acid, and then passing a current of pure dry chlorine into the solution until the titration figure with thiosulphate, after the addition of potassium iodide, has been doubled; the solution becomes distinctly lighter in shade at this point. Care should be taken not to have excess of chlorine as it has been pointed out by several observers that the Wijs solution in order to give accurate results should have a slight excess

of iodine over chlorine. Ueno (*J.S.C.I.*, 1916, 35, 367); Schmidt-Nielsen and Owe (*J.S.C.I.*, 1924, 43, B302). See also page 138.

In order to get over the difficulties of using acetic acid as the solvent, Hildt has suggested (*J.S.C.I.*, 1919, 38, 589A) the use of carbon tetrachloride in its place. Although the writer has not, as yet, made any comparative tests of the two methods the results obtained by the use of the tetrachloride have been quite normal. The method is well worth extended trial as it has obvious advantages.

The Hanus Method.—This method is similar to that of Wijs, the active agent being iodine bromide in place of the iodine chloride of the former. At the time the suggestion was made the great advantage lay in the comparative ease with which the solution could be made up, but this is no longer of any great importance since it has been possible to purchase iodine monochloride quite cheaply as such. The method is described below for the purpose of completeness, but in so far as it offers no material advantages over the Wijs method, and as so many results have already been obtained by using the latter method there is no object in increasing the confusion already existing by the use of another method. Moreover, some writers have asserted that the results obtained by the two methods are not identical, although this is not accepted by all. (Cf. A. Marshall, *J.S.C.I.*, 1900, 19, 213; T. F. Harvey, *J.S.C.I.*, 1902, 21, 1437; 1904, 23, 306; L. Archbutt, *J.S.C.I.*, 1904, 23, 306). The Hanus method is, however, strongly recommended by Holde and his co-workers (*J.S.C.I.*, 1922, 41, 557A). The influence of the solvent on the Hanus value has been considered by Bankston and Vilbrandt (*J.S.C.I.*, 1924, 43, 681B).

Prepare the reagent by adding 13 grms. of bromine (cf. the work of Radcliffe and Polychronis below, p. 142) drop by drop to 20 grms. of finely-powdered iodine which is kept at a low temperature by means of ice. The process is carried through with the same technique as that used for the Wijs process, the time of contact varying from 15 minutes to an hour according to the degree of unsaturation of the oil.

Manchot and Oberhauser (*J.S.C.I.*, 1924, 43, 564B) found that excellent agreement with iodine values determined by Hübl's method for substances of iodine value varying from that of oleic acid to that of linolenic acid was obtained by using the following bromine solutions: (*a*) 0·1 N bromine in 20 per cent. hydrochloric acid solution with 10 c.c. of chloroform for each determination; (*b*) bromine in commercial 99–100 per cent. acetic acid with the addition of chloroform; (*c*) bromine in acetic acid solution without the addition of chloroform. In carrying out the determination, 10 c.c. of chloroform are added to a weighed amount of the substance, the iodine value of which is to be determined, in a stoppered flask, and excess of the bromine solution is added. After allowing the flask to stand for a suitable period of time in the dark, sufficient arsenious acid solution is added to render it colourless, the solution diluted to 2–3 times its volume, and titrated with bromine solution, using indigo carmine or a mixture of equal parts of indigo carmine and trinitroresorcinol as indicator. The reaction periods necessary for linolenic acid and the three bromine solutions specified above are (*a*) 4 hrs., (*b*) 3 hrs., and (*c*) 24 hrs. (Cf. Holde and Gorgas, *J.S.C.I.*, 1925, 44, B600.)

Winkler's Method.—Winkler's method consists in the use of 50 c.c. of a N/10 solution of potassium bromate solution which contains about 1 grm. of potassium bromide and 10 c.c. of 10 per cent. hydrochloric acid, the oil being dissolved in 10 c.c. of carbon tetrachloride as usual. The absorption is allowed to continue in the dark for one or two hours, according to the

degree of unsaturation of the oil, potassium iodide is added and the titration continued as usual. St. Weiser and Donath (*Analyst*, 1914, 39, 406) find that the results obtained by this method agree closely with those obtained by the methods of Hübl, Waller and Wijs.

The method is stated by Kelber and Rheinheimer (*Analyst*, 1918, 43, 90) to give low results in the case of oils with high iodine value, and the same conclusion is reached by Sundberg and Lundborg (*Analyst*, 1920, 45, 338), but Lakhani and Sudborough (*J.S.C.I.*, 1920, 39, 341A) state that the method is trustworthy in the absence of light, and report that the use of bone charcoal increases the rate of absorption. (Cf. E. Schulek, *J.S.C.I.*, 1921, 40, 593A; L. Winkler, *J.S.C.I.*, 1922, 41, 473A; 1924, 43, B755; O. Köpke, *J.S.C.I.*, 1925, 44, B105; K. Scheffler, *ibid.*, p. B728.)

Aschman's Method.—This method (*Chem. Zeit.*, 1898, 22, 59) depends upon the use of an aqueous solution of iodine monochloride in place of the acetic acid solution of Wijs. This solution, which is prepared by the action of an aqueous solution of chlorine or an aqueous solution of potassium iodide is used exactly as is that of Wijs. Margosches and Baru (*J.S.C.I.*, 1921, 40, 779A) report that the results obtained by this method agree closely with those obtained by the methods of Wijs and Hübl, although the time required for absorption is about 24 hours. (Cf. E. Stock, *J.S.C.I.*, 1926, 45, B20.) These authors (*J.S.C.I.*, 1921, 40, 856A) subsequently published a modified process which may be carried out as follows:

15 grms. of potassium iodide is dissolved in 50 c.c. of water, and chlorine is passed through until the iodine, at first precipitated, is completely redissolved. The solution is allowed to stand for five hours and is then decanted from the crystalline precipitate, which is washed, and the solution and washings made up to 500 c.c. with water. (This solution is even more stable than Wijs' solution.) About 0·5–0·1 grm. of the oil or fat (according to the iodine value expected) is dissolved in 10 c.c. of carbon tetrachloride, and 10 c.c. of the iodine monochloride solution added. The mixture is then shaken, and the shaking is repeated two or three times during the first half of the absorption period, which varies from 2 to 4 hours for fats, 6 hours for non-drying, 8 hours for semi-drying, and 24 hours for drying oils, when only 60 per cent. excess of iodine is used. The time can be reduced by using a larger excess (75 per cent.) when 6–8 hours is sufficient even for drying oils. The excess of iodine is titrated in the usual way.

Subsequently, the same authors showed (*Analyst*, 1923, 48, 346) that a solvent need not be used and neither is shaking necessary if the time of contact be at least 24 hours.

B. M. Margosches (and his co-workers) has recently introduced (*J.S.C.I.*, 1925, 44, B410, B600) what he terms the " upper iodine value," that is to say, the iodine absorption after 24 hours in aqueous-alcoholic solution as compared with the absorption under the same conditions in five minutes. He claims that the five minutes value corresponds to the Hübl value and that the difference between this and the 24 hour value has diagnostic properties. Thus the Hübl values for olive and castor oils are similar, the " Upper Iodine Values " are 119·7 and 162·2 respectively. Similar useful results are recorded with poppy and sunflower oils, sesamé and cotton-seed oils, almond and rape oils.

The Pyridine Method.—K. W. Rosenmund and W. Kuhnhenn (*J.S.C.I.*, 1924, 43, 23B; 1925, 44, B214) have proposed the use of a solution of pyridine sulphate dibromide in glacial acetic acid. The advantages claimed are speed of absorption and need for only slight excess. A N/10 solution of the reagent is prepared by dissolving separately 8 grms. of pyridine and 10 grms. of

concentrated sulphuric acid in 20 c.c. of glacial acetic acid, adding 8 grms. of bromine dissolved in 20 c.c. of glacial acetic acid, and diluting the whole with glacial acetic acid to 1 litre. The reaction is complete in 5 minutes, even in the case of linseed oil, and the results obtained agree with those given by the Hanus method within the limits of experimental error. The excess of reagent can either be treated with potassium iodide and titrated with thiosulphate, or titrated direct with arsenious acid, the two methods giving identical results. Winkler (*J.S.C.I.*, 1925, 44, B138) considers that no advantage is obtained by the addition of pyridine, but this is not accepted by the authors of the process (v.s.). (Cf. W. Müller, *J.S.C.I.*, 1925, 44, B640; and B. Bierert, *ibid.*, p. B929).

A Direct Method.—Sabalitschka and Dietrich (*J.S.C.I.*, 1924, 43, B525) spread 0·1 to 0·4 grm. in a thin film on glass and weigh. They then place the film of oil thus prepared in a stoppered horizontal cylinder containing a few drops of bromine for one hour at the ordinary temperature. The bromine dissolved by the oil is then expelled by heating the glass plate for two to three hours at 60°. The plate and oil are then again weighed and the iodine value calculated from the increase in weight. These authors found that the values so obtained show fairly satisfactory agreement with the Hübl method and even in the case of linseed oil the discrepancy was less than 2 per cent.

The Relationship of the Various Methods.—As a general rule the iodine value obtained does not depend to a large extent on the method used, but the variations which have been obtained cannot be ignored and it is desirable that some standard method should be adopted; failing this it is necessary to state the process by which the value has been determined in all cases where uncertainty is likely to arise.

Auguet (*J.S.C.I.*, 1912, 31, 1137), commenting upon the somewhat lower results frequently obtained by the Hübl process as compared with the Wijs, states that this may be overcome by the addition of a little hydriodic acid to the former and states that the results do not differ by more than 1 per cent. when the iodine value is less than 130.

Radcliffe and Polychronis (*J.S.C.I.*, 1916, 35, 340) examined in some detail the methods of Hübl, Hanus and Wijs as applied to the determination of the iodine values of hydrocarbon oils. They found that very slight differences in the amount of bromine used in making up the solution for the Hanus method led to varying results being obtained, so that they abandoned this; they further found that the results obtained by the other methods depended to a considerable extent on the temperature of the solutions and on the time of contact, further absorption taking place after twenty-four hours. The Wijs method gave results of the order of three times those obtained by the Hübl method. It was further found that isopentane absorbed no iodine and that isoamylene absorbed 35·7 per cent. by the Wijs method, the theoretical figure being 36·3 per cent., an excellent result.

Kelber and Rheinheimer (*Analyst*, 1918, 43, 90) state that the Hübl and Wijs methods give concordant results; they prefer the Wijs. The Winkler method was found to give low results with oils of high iodine value. Sundberg and Lundborg (*Analyst*, 1920, 45, 338) state that the Hanus method yields results which agree closely with those found by the Hübl method; the Wijs method gives higher results and the Winkler method lower results. They state that in the case of linolic acid the Hübl value lies nearer to the theoretical iodine value than does the Wijs value, but as the purity of such an acid is certainly open to doubt this might be used to show the advantage of the Wijs method. The same remarks apply to the work of W. Devrient (*J.S.C.I.*, 1920, 39, 755A), who found the iodine value of a sample of elaidic

acid by the Hübl, Waller, Winkler and Wijs methods to be 80·3, 80·0, 80·8 and 80·8 respectively, whilst that by the Hanus method was 82·5. He prefers the latter method merely because the result is nearer to the theoretical value of 90, but the balance of this evidence is obviously against it.

MacLean and Thomas (*J.S.C.I.*, 1921, 40, 518A) state that for a fat containing appreciable quantities of sterols, the Hübl value more accurately expresses the degree of unsaturation than that of Wijs. This opinion is confirmed to a certain extent by Holde, Werner, Tacke and Wilke (*J.S.C.I.*, 1922, 41, 557A), who also prefer the Hanus reagent and who state that the Wijs solution gives values for sterols of about twice the theoretical. The difficulty of obtaining pure substances may, however, have something to do with these results. E. André (*J.S.C.I.*, 1924, 43, B139) placed solutions of iodine in carbon tetrachloride, carbon bisulphide, chloroform and acetic acid respectively in contact with olive, sesamé, poppy and cod-liver oils and also with isoheptone and phenylbutyline. The amount of iodine fixed in each case was determined, and the results obtained were expressed as a fraction of the iodine value. The violet solutions in carbon tetrachloride and carbon bisulphide are less active than the red or brown solutions, but the reaction appears to give very variable results even when experimental conditions are apparently similar. (Cf. J. J. Cerdeiras, *J.S.C.I.*, 1924, 43, B838; T. Sundberg, *ibid.*, 1925, 44, B679; and P. Gillot, *ibid.*, 1925, 44, B679).

The Method Recommended.—For ordinary work the Wijs method has many advantages and should be adopted; it is generally used in this country. Although other methods are used in other countries (the Hanus method is the official method of the American A.O.A.C.) the use of the Wijs method is extending and it is quite likely that it may be universally recognised. Doubtless the results obtained are not always " theoretical " but they have the great advantage of being concordant and until some absolute method is devised the Wijs method is able to give all the information really necessary.

The Bromine Value

A method for the determination of the bromine absorption value of fats was first proposed by Mills, Snodgrass and Akitt (*J.S.C.I.*, 1883, 2, 435; 1884, 3, 366). The method was based upon the addition of a dilute solution of bromine in carbon tetrachloride to a solution of about 0·1 grm. of the fat in the same solvent until an excess of bromine persisted for fifteen minutes, the excess of bromine then being titrated with thiosulphate after the addition of potassium iodide.

During the absorption a certain amount of hydrobromic acid is produced indicating that substitution has also been taking place. The hydrobromic acid so produced may be titrated and the substituted bromine so determined subtracted from the total used thus giving the actual amount of " added " bromine. A method using these principles has been worked out by M'Ilhiney (*J.S.C.I.*, 1894, 13, 668).

Using a similar method W. Vaubel (*Analyst*, 1911, 36, 19) observed that when an oil is dissolved in carbon tetrachloride with the addition of potassium bromide and hydrochloric acid, and the solution is then titrated with potassium bromate solution, the quantity of bromine taken up by the oil is not equivalent to the iodine value of the oil. Further experiments showed that non-drying oils, such as olive oil, absorb little, if any, bromine when thus treated; whilst drying oils absorb the bromine readily up to a certain point, where the addition of a further quantity of bromate solution produces a yellow colour of free bromine in the solution. The quantity of bromine

thus absorbed by the oil is termed the " primary bromine value." Only when an excess of bromine is added does the oil absorb a quantity equivalent to the iodine value, and this quantity is called the " secondary bromine value " of the oil. The following values were obtained in the case of three oils : Linseed oil, primary value, 75·2, 80·0; secondary value, 107·7. Wood oil, primary value, 57·0; secondary value, 94·6. Earthnut oil, primary value, 51·9; secondary value, 57·6. The author discusses the relation between these results and the compositions of the oils. For the determination of the total (secondary) bromine values of oils, the author recommends that 5 grms. of the oil be dissolved in 100 c.c. of carbon tetrachloride; potassium bromide solution and about 300 c.c. of water are added, then 10 c.c. of concentrated hydrochloric acid and a small crystal of potassium iodide. After the addition of an excess of standard potassium bromate solution, the mixture is shaken thoroughly for one minute, and the excess of bromine is then titrated with sodium sulphite solution. The small quantity of iodine added in the form of potassium iodide enables the end point of the titration to be observed clearly. The results obtained, when calculated into terms of iodine are stated to agree closely with the iodine values of the various oils as estimated in the usual way.

Gravimetric methods have been suggested by various workers, but in general these are not reliable. Cf. Waller (*Analyst*, 1895, 20, 280); Lewkowitsch (*J.S.C.I.*, 1896, 15, 859); Jenkins (*J.S.C.I.*, 1897, 16, 193); Procter and Bennett (*J.S.C.I.*, 1906, 25, 799). A method given by Becker (*J.S.C.I.*, 1923, 42, 1185A) and by Sabalitschka and Dietrich (*J.S.C.I.*, 1924, 43, B525) is described under iodine value on page 142. R. Biazzo (*J.S.C.I.*, 1924, 43, B478) has described a process in which the fat is dissolved in chloroform and the solution cooled with running water at 15°, whilst a chloroform solution of bromine (1 : 1) is added, drop by drop, until a permanent brick-red colour is obtained. The excess of bromine and the chloroform are removed by passing a current of dry carbon dioxide through the liquid heated to 100°. The liquid is allowed to cool in a current of carbon dioxide and weighed.

In general, however, the bromine value is no longer used. It has been almost entirely superseded by the iodine value which gives more trustworthy results. In view of the almost universal application of the iodine value it is unlikely that the bromine value will be revived; it will be necessary to show material advantages before such a thing would be generally accepted. (Cf. the pyridine method, page 141.)

A new suggestion has lately been made by H. P. Kaufmann (*Analyst*, 1925, 50, 577) in which the reagent used for the titration is a solution of a thiocyanogen compound in glacial acetic acid. The amount of thiocyanogen added to an unsaturated oil or fatty acid does not correspond to the iodine value; there may be partial or complete absorption, or none at all. The behaviour of linolic acid and its triglyceride is the most interesting, the thiocyanogen radicle being only absorbed at one double bond. Hence, by determining the iodide value and the thiocyanogen value of an oil it is possible to obtain, from the difference between the two values, the amounts of the respective unsaturated constituents present. Details of the procedure are to be published. Cf. *Analyst*, 1926, 51, 157; 1925, 50, 634.

The Reichert Process and its Modifications

After Hehner and Angell had shown that the great difference between butter fat and all other fats was the comparatively large amount of butyric acid which was contained in the former, they endeavoured to determine the

amount by a distillation method, but they were unable to obtain concordant results and they finally gave up the method in favour of the determination of the soluble and insoluble acids. (*Butter and its Adulteration*, 1879). This method is given here as described by the American A.O.A.C., it is not, however, used now to any great extent having been superseded by more modern methods.

Determination of Soluble and Insoluble Acids (*Hehner*) *after A.O.A.C.*:

(*a*) *Soluble Acids.*—Evaporate the neutralised liquid obtained from the saponification value (page 117) to dryness on the water-bath. Add such an amount of N/2 hydrochloric acid that its volume plus the amount used in

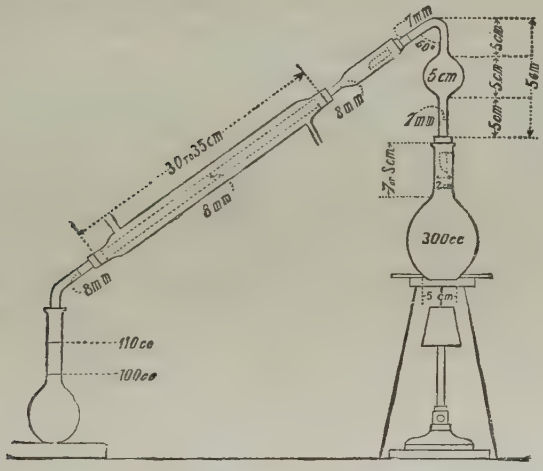

FIG. 3.—Reichert Apparatus

[*By permission of Baird & Tatlock (London) Ltd.*

titrating for the saponification number will be 1 c.c. in excess of the amount required to neutralise the 50 c.c. of the alcoholic potassium hydroxide solution added, and place on the steam-bath until the separated fatty acids form a clear layer on the upper surface of the liquid. Fill to the neck with hot water and cool in ice water until the cake of fatty acids is thoroughly hardened. Pour the liquid contents of the flask through a filter into a litre flask. Fill the flask again with hot water, set on the steam-bath until the fatty acids collect at the surface, cool by immersing in ice water, and again filter the liquid into the litre flask. Repeat this treatment with hot water three times, cooling and collecting the washings in the litre flask after each treatment. Titrate the combined washings with N/10 alkali, using phenolphthalein as an indicator. Subtract 5 (corresponding to the excess of 1 c.c. of N/2 acid) from the number of c.c. of N/10 alkali used, and multiply by 0·0088 to obtain the weight of soluble acids as butyric acid. Calculate the percentage of soluble acids.

(*b*) *Insoluble Acids.*—Allow the flask containing the cake of insoluble fatty acids from the previous determination and the paper through which the soluble fatty acids have been filtered to drain and dry for 12 hours. Transfer the cake, together with as much of the fatty acids as can be removed from the filter-paper, to a weighed, wide-mouthed beaker flask. Then place the funnel, containing the filter, in the neck of the flask and wash the paper

thoroughly with hot absolute alcohol. Remove the funnel, evaporate off the alcohol, dry for 2 hours at 100° C., cool in a desiccator and weigh. Again dry for 2 hours, cool and weigh. If there is any considerable decrease in weight, re-heat for 2 hours and weigh again. Calculate the percentage of insoluble fatty acids.

The Original Reichert Process.—The experiments of Hehner and Angell were continued by Reichert (*Zeit. Anal. Chem.*, 1879, 18, 68), who proposed a distillation method using 2·5 grms. of fat and saponifying the fat with alcoholic potash. The actual method is as follows:

2·5 grms. of the filtered fat are weighed into a small flask fitted with a cork, through which passes a short piece of glass tubing, and saponified by adding 5 c.c. of pure alcohol and 6 c.c. of a concentrated aqueous solution of potassium hydroxide (free from carbonate), and heating on the water-bath for a short time. After expelling all traces of alcohol, the dry soap is dissolved in 70 c.c. of boiling water, and the fatty acids liberated by adding 5 c.c. of sulphuric acid of the right strength to neutralise the alkali. The liquid is then gently distilled * until exactly 50 c.c. have passed over. This distillate is filtered, the filter washed with boiling water, and the filtrate and washings titrated with decinormal solution of potassium or barium hydroxide. The number of c.c. required is the Reichert value.

The following table due to Allen (*Commercial Organic Analysis*) gives the results obtained by this method on a number of fats.

TABLE XXXIX.—RESULTS FROM REICHERT PROCESS (ALLEN)

Substance.	Reichert. 2·5 grams.
Milk Fats—	
Cow's butter	12·5–15·2
Ewe's butter	13·7
Goat's butter	13·6
Porpoise's butter	11·3
Animal and Vegetable Oils and Fats—	
Coconut oil †	3·5–3·7
Palm-kernel oil	2·4
Palm oil	0·8
Cacao butter	1·6
Margarine and oleomargarine	0·2–1·6
Whale oil	3·7–12·5
Porpoise oil	11–12
Sperm oil	1·3
Bottle-nose oil	1·4
Menhaden oil	1·2
Cod-liver oil	1·1–2·1
Sesamé oil	2·2
Cotton-seed oil	0·3
Castor oil	1·4

* To avoid bumping, pumice-stone with platinum wire coiled round should be placed in the distilling vessel.

† By adding more water and continuing the distillation, a large amount of solid fatty acid, mostly insoluble in water (chiefly lauric acid), can be distilled over in the case of coconut oil.

The Modifications of Meissl and Wollny.—Meissl (*Dingler's polyt. J.*, 233, 229) modified the test by using 5 grms. of fat, distilling 110 c.c., filtering and titrating. The method was examined at length by Wollny (*Analyst*, 1887, 12, 203, 235; 1888, 13, 8, 38) who found that errors might creep into the process due to:

(1) Absorption of carbon dioxide during the process.
(2) Formation of esters during saponification.
(3) Formation of esters during distillation.
(4) Cohesion of the fatty acids during distillation.
(5) Variations in the size and shape of the distillation apparatus and in the time of distillation.

The modified method of Wollny (sometimes called the Reichert-Wollny method but, as the other methods have entirely fallen into disuse, the shorter term Reichert method adopted in this book would seem to have advantages) was adopted by the Joint Committee of the Government Laboratory and the Society of Public Analysts and described by them as follows:

Five grms. of liquefied fat are introduced into a 300 c.c. flask, of the form shown (length of neck 7 to 8 centimetres, width of neck 2 centimetres). Two c.c. of a caustic soda solution, prepared by dissolving 98 per cent. sodium hydrate in an equal weight of water—protected from the action of atmospheric carbonic acid—and 10 c.c. of (about 92 per cent.) alcohol are added, and the mixture is heated for fifteen minutes under a reflux condenser, connected with the flask by a T-piece, in a bath containing boiling water. The alcohol is evaporated off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water which have been kept boiling for at least ten minutes (to drive out all dissolved carbonic acid, the retention of which would vitiate the result) are added, and the flask is heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide, and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre, 5 centimetres in diameter, and is first heated by a very small flame, to fuse the insoluble fatty acids, but the heat must not be so great as to cause the liquid to boil; when fusion is complete, the heat is increased,* 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (from 28 to 32 minutes). The distillate is shaken, 100 c.c. are filtered in a flask, 0·5 c.c. of phenolphthalein solution (1 grm. in 100 c.c. alcohol) is added, and the filtrate titrated with decinormal soda or baryta solution. In precisely the same manner (with the same reagents), a blank test should be made, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained in the blank experiment, is multiplied by 1·1. The number so found is the Reichert-Wollny value.

Further modifications which have been suggested will be dealt with under the Polenske process as the type of still used by Polenske is now generally used in the Reichert process, the values obtained by the two methods (for the Reichert process *not* for the Polenske process) being practically

* The heating of the asbestos plate itself should be guarded against, as serious errors arise if the asbestos should become overheated.

identical. The use of 4 c.c. only of glycerol has been recommended by H. Kreis (*Analyst*, 1911, 36, 542), but such a small quantity is not easily manipulated.

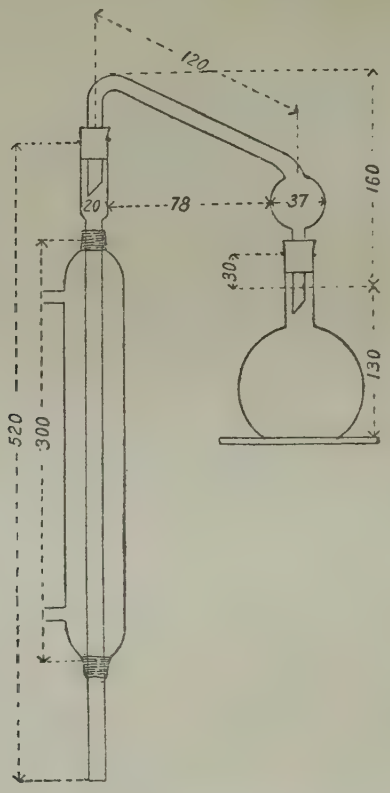

FIG. 4.—Polenske Apparatus

[*By permission of Mr J. A. L. Sutcliffe*

The Polenske Process.—The method of Reichert depends upon the determination of the soluble volatile acids, that of Polenske on the determination of the insoluble volatile acids. The idea seems to have been first considered by Salkowski (*Zeit. f. Analy. Chem.*, 1887, 26, 581) but was worked out independently by Muntz and Coudon (*Analyst*, 1905, 30, 155) and by Polenske (*Analyst*, 1904, 29, 154). The latter has been the method preferred in this country; it is carried out as follows (Revis and Bolton, *Analyst*, 1911, 36, 335) :

Five grms. of the fat and 20 grms. of glycerol are weighed with a 300 c.c. flask, and 2 c.c. of 50 per cent. sodium hydroxide solution added. The flask is heated over a flame with constant shaking till it clears suddenly, the soap is then cooled and 100 c.c. of recently well-boiled distilled water is added, until solution of the soap is effected. 0·1 grm. of powdered pumice sieved through butter muslin is added, and then 40 c.c. of sulphuric acid solution (20 to 25 c.c. of strong sulphuric acid diluted to 1000 c.c. and the solution adjusted so that 35 c.c. neutralise 2 c.c. of the sodium hydroxide solution). The flask is at once connected with the condenser, and heated with a small flame till the insoluble acids are completely melted; the flame

is then increased, and 110 c.c. distilled in nineteen to twenty-one minutes. The temperature of the condenser water should be from 18° to 20° C., and the dimensions of the apparatus are to be the same as given by Polenske. When 110 c.c. have distilled, the flame is removed, and a 25 c.c. cylinder placed under the condenser to catch any drops. The 110 c.c. flask and contents are stood in water at 10° to 15° C. for fifteen minutes. After mixing the contents of the 110 c.c. flask, they are filtered and 100 c.c. titrated with N/10 baryta, using 0·5 c.c. of a 1 per cent. solution of phenolphthalein as indicator. This number of c.c. increased by one-tenth, after subtraction of the blank (which must be determined in an exactly similar way, by using all the reagents except the fat), is the Reichert-Meissl value. The condenser, cylinder, and 110 c.c. receiver, are washed with 18 c.c. of cold water, which are then poured over the filter used to filter the distillate, and rejected. The condenser is washed out with four successive portions of 10 c.c. of neutral alcohol, which are received in the cylinder and poured over the filter into the 110 c.c. flask, the mixed alcohol solutions being then titrated with N/10 baryta using phenolphthalein as an indicator. A blank value is obtained in a similar way. The number of c.c. of N/10 baryta used, less the number used for the blank, is the Polenske figure.

When carrying out this process, which may be described as the Reichert-Polenske process and which is the method now almost universally employed, it is most necessary that the exact conditions be complied with. Richmond and Hall (*J.S.C.I.*, 1920, 39, 80T) have shown that, although a slight difference in the temperature of the distillate is not of serious moment, it is most necessary to adhere strictly to the *time* of distillation in those cases where material quantities of coconut oil are present. The quantity and size of the pumice is also of serious moment and Bolton, Richmond and Revis (*Analyst*, 1912, 37, 185) have shown that the position of the hole in the side of the still-head is of importance; it should not be more than about 1 cm. from the lower end of the stopper.

The effect of pressure upon the determination has been studied by V. H. Kirkham (*Analyst*, 1920, 45, 293), who states that while the Reichert value is a logarithmic function of the pressure, and the errors introduced by ordinary variations in the atmospheric pressure are quite small, the Polenske value is a function of the pressure and quite serious errors are likely to be introduced. The following figures were found :

TABLE XL.—COMPARISON OF REICHERT AND POLENSKE VALUES (KIRKHAM)

Pressure. mm.	Reichert-Meissl.		Polenske.	
	Found.	Calculated.	Found.	Calculated.
100 . . .	22·34	22·58	0·19	0·19
180 . . .	24·43	24·19	0·48	0·48
250 . . .	25·57	25·10	0·75	0·73
380 . . .	26·93	26·23	1·14	1·19
450 . . .	27·13	26·69	1·61	1·44
627 . . .	27·60	27·60	2·06	2·07
760 . . .	27·99	28·12	2·68	2·55
900 . . .	28·17	28·60	..	..
1000 . . .	28·05	28·87	3·40	3·40

Kirkham suggests that where the barometric pressure differs seriously from the normal the following correction be applied :

$$V = \frac{v(P-K)}{p-K}$$

where p is the pressure at which Polenske value is V, p is the pressure at which Polenske value is v and K is a constant, or pressure at which the Polenske value is 0, in this case 45. Such a correction will only become serious in those cases where work is carried out at a barometric pressure differing considerably from 760 mm. Earlier investigations on the Polenske process and its modification which have now been replaced by the process described above have been made by A. W. Thorp (*Analyst*, 1906, 31, 173), Rideal and Harrison (*Analyst*, 1906, 31, 254), F. W. Harris (*Analyst*, 1906, 31, 353), Tatlock and Thomson (*J.S.C.I.*, 1909, 28, 69), W. Arnold (*Analyst*, 1912, 37, 256), Barthel and Sonden (*Analyst*, 1914, 39, 254). A modification by Cassal and Gerrans (*Analyst*, 1910, 35, 519) is discussed under coconut oil on page 335.

W. Arnold (*J.S.C.I.*, 1922, 41, 181A) has carried out experiments with pure acids with the idea of finding which of them contribute materially to the Polenske value. He found that butyric and caproic yield only soluble acids, caprylic and capric acids give both Reichert and Polenske figures, whilst lauric and the higher acids give only Polenske figures. Of the insoluble acids capric and lauric acids are easily volatile, palmitic and stearic acids volatile with difficulty, myristic acid standing midway between the two groups.

Several workers have studied the relationship which exists between the Reichert and the Polenske values in the case of butter fat. This question is discussed on page 335.

The Polenske values of the fats usually lie well under 1·0 even in the case of rancid fats which frequently give abnormally high Reichert values (cf. J. E. Southcombe, *J.S.C.I.*, 1909, 28, 499). Thus the following results were obtained by Elsdon (*Y.B.P.*, 1913, 575):

Table XLI.—Polenske Values (Elsdon)

Oil.	Acidity. % KOH.	Reichert.	Polenske.
Cotton-seed . . .	4·04	11·1	0·6
Menhaden	5·04	11·0	0·9
Cod-liver	1·02	4·6	0·6
Brusmer	2·63	8·2	0·6

The oil of soya-bean miso (*J.S.C.I.*, 1924, 43, 564B), a Japanese food prepared by the fermentation of soya-beans, had Reichert value 3·6–7·5 with a saponification value of 211–235.

A large number of the high Reichert figures given in literature were obtained with rancid oils and so are valueless for use in the examination of normal oils. Such figures, where any doubt occurs, have been ignored in the following table which contains the average figures generally accepted. It may be necessary to extend this list further as new oils are discovered or old oils are reinvestigated.

TABLE XLII.—AVERAGE FIGURES

Fat.	Reichert.	Polenske.	Kirschner.	Saponification Value.
[18] Myrtle seed	9	..	..	200
Croton	13	1·2	..	212
Butter	28	2·7	24	228
Spindle-tree	35	..	..	230
[8] Dolphin, body	35	..	..	225
[8] ,, jaw	112	..	..	280
Porpoise, body	60	..	..	240
[21] ,, jaw	130	..	..	260
Macassar oil	9	..	..	220
Muriti	5	..	..	246
Mocaya	7	12	..	245
[1] Areca nut	4·2	..	..	230
Maripa	5	..	..	260
Palm-kernel	5·5	5·5	1·0	250
Coconut	7	17	1·9	255
Tonka	5	..	..	257
[2] Akebi seed	39·8	..	..	246
[3] Mapia seed	45·0	0·5	26·7	237
[4] Cheyi seed	45·6	..	..	251
[5] Curua palm	6·3	15·6	..	260
[6] Balanites tæghemi	6·0	..	..	..
[6] Saccoglottis gabonensis	5·5	..	..	188
[7] Melia azadirachta	8·3	0·3	5·0	186
[7] Schleichera trijuga	16·0	0·3	14·5	227
[9] Trichilia subcordata	3·3	..	..	201
[9] Manihot glazcovii	10·7	..	..	193
[10] Pentaclethra macrophylla	6·5	0·5	..	182
[11] Coyol palm	5·0	..	..	246
[12] Onigurumi seed	4·9	..	..	188
[13] Lindera obstiroba	2·6	9·9	..	264
[14] Mafura fat	3·2	2·7	..	204
[15] Elm seed	3·8	..	..	277
[16] Hakuunboku	16·4	..	..	182
[17] Magnolia fruit	4·7	..	..	224
[19] Dika	..	5·5	..	242
[20] Ochoco	..	4·0	..	239

[1] *Analyst*, 1909, 34, 64. Extracted with petroleum ether. Nut extracted with ether had R=0·2. [2] *J.S.C.I.*, 1916, 35, 1091. [3] *Analyst*, 1922, 47, 282. [4] *J.S.C.I.*, 1913, 32, 496. [5] *Analyst*, 1921, 46, 50. [6] *J.S.C.I.*, 1911, 30, 497. [7] *Analyst*, 1915, 40, 3. [8] *J.S.C.I.*, 1913, 32, 433, 612. [9] *J.S.C.I.*, 1914, 33, 147, 322. [10] *J.S.C.I.*, 1914, 33, 1098. [11] *J.S.C.I.*, 1915, 34, 1061. [12] *J.S.C.I.*, 1916, 35, 262. [13] *J.S.C.I.*, 1921, 40, 856A. [14] *J.S.C.I.*, 1922, 41, 21A. [15] *Analyst*, 1912, 37, 201. [16] *J.S.C.I.*, 1916, 35, 1091. [17] *J.S.C.I.*, 1916, 35, 1092. [18] *Analyst*, 1907, 32, 366. [19] *Analyst*, 1912, 37, 349. [20] *Analyst*, 1908, 33, 313. [21] *J.S.C.I.*, 1890, 9, 331. (Cf. also *J.S.C.I.*, 1916, 35, 1092, 261; 1919, 38, 426A; 1911, 30, 140; 1920, 39, 346A; 1923, 42, 276A. *Analyst*, 1908, 33, 423, 184, 189; 1909, 34, 10; 1914, 39, 134; 1921, 46, 325.)

The Reichert value of fats may be increased artificially by the addition of such substances as triacetin and tributyrin. These may be detected by extracting the fat with 70 per cent. alcohol, when the extracted fat will have a lower Reichert value than the original fat in cases where artificial esters are present (*Analyst*, 1909, 34, 50).

The presence of preservatives such as benzoic acid, etc., will tend to increase the Reichert value. E. Bemelmans (*Analyst*, 1907, 32, 218) states that benzoic acid has a comparatively greater effect than salicylic acid. C. Grimaldi (*Analyst*, 1908, 33, 397; 1913, 38, 68) states that the effect of salicylic acid may be disregarded, whilst that of benzoic is usually quite small. In cases where any doubt arises, and the presence of benzoic acid has been discovered, it may be removed by shaking the molten fat with successive quantities of very dilute sodium carbonate solution before the Reichert figure is determined.

The melting-point of the insoluble acids obtained in the Reichert-Polenske process has been studied by various workers. It was first seriously suggested by Blichfeldt (*J.S.C.I.*, 1919, 38, 150T) and the work has been extended by Stokoe (*J.S.C.I.*, 1921, 40, 57T) as a means of distinguishing between coconut and palm-kernel oils, and by Gilmour (*Analyst*, 1921, 46, 183) as a method for the analysis of butter with the object of detecting adulteration. Some of the results of Stokoe are given under butter fat on page 337; Gilmour found that the melting-points of the Polenske acids from pure butter fats lie between 15·8° and 25·6°. " Butter with high total and insoluble volatile figures usually have low melting-points above 15·8°, but if the total volatile figure falls below 28°, then the melting-point should be above 20·0°."

Combined Esterification and Distillation Methods.—Fox and Wanklyn (*Analyst*, 1884, 9, 73) suggested a method for the examination of butter, based upon the formation of butyric ester during " restricted " saponification. This idea has been utilised by Hanus (*Analyst*, 1907, 32, 89; 1908, 33, 281; 1911, 36, 106) and by Fendler (*Analyst*, 1910, 35, 355). These methods at present show no advantage over the Reichert-Polenske methods generally adopted—they are described below, however, as they make use of principles which may be of value in other directions.

(*a*) *The Hanus Ester Method.*—This method is carried out as follows: Five grms. of the melted fat are placed in a flask and heated for fifteen minutes in an oven at 50°; exactly 30 c.c. of N/10 alcoholic potassium hydroxide solution are then added from a burette, and the mixture is thoroughly shaken until perfectly clear, usually about two minutes. After keeping the contents of the flask at a temperature of 50° for a further eight minutes, 2 c.c. of dilute sulphuric acid are added, the acid being of such concentration that the 2 c.c. will exactly neutralise the 30 c.c. of potassium hydroxide solution. The contents of the flask are now diluted to a volume of 145 c.c. with water, a few pieces of pumice are added, and the mixture is distilled. The first 30 c.c. of alcoholic distillate which comes over is collected in a graduated cylinder, the next 100 c.c. of distillate being received separately in a 100 c.c. flask. The whole distillation must not take longer than forty-five minutes. Both fractions of the distillate are now transferred to two flasks; alcohol is added to the aqueous distillate until a clear solution is obtained, the free acidity of both portions is neutralised, and they are then boiled with an excess of N/10 alcoholic potassium hydroxide solution. On titrating back the excess of alkali, the number of c.c. of N/10 alkali required for the saponification of the esters from 5 grms. of the fat is obtained. The following results obtained by the method are recorded:

TABLE XLIII.—RESULTS OF HANUS ESTER METHOD

Kind of Fat.	c.c. N/10 Alkali required for Saponification of the Esters.	
	Alcoholic Portion.	Aqueous Portion.
Butter, No. 1	24·60	9·05
,, No. 2	25·80	8·05
,, No. 3	26·20	9·40
Crude coconut oil	10·65	41·45
Coconut oil, Cochin	17·20	40·10
,, ,, Ceres, No. 1	13·80	42·80
,, ,, ,, No. 2	11·05	43·90
,, ,, ,, No. 3	13·60	38·20
Butter, No. 2, plus 5 per cent. coconut oil	26·00	11·20
,, ,, ,, 10 ,, ,, ,, ,,	25·80	14·90
Lard	0·60	1·60
,, plus 7 per cent. coconut oil	2·00	4·50

The amount of alkali, expressed in c.c. of N/10 solution, is termed the " ethyl ester value " of the fat. In the case of butter, this value lies between 7 and 14; for coconut oil it is upwards of 40, whilst for all other commonly occurring fats it is less than 3. Owing to the variations of the value in the case of pure butters, a less quantity than 15 per cent. of coconut oil cannot be detected with certainty in butter. (Cf. J. Lukas, *J.S.C.I.*, 1925, 44, B929.)

b. The Fendler Method.—This method (*Analyst*, 1910, 35, 355) is founded on that of Henriques (*Analyst*, 1898, 23, 181); it is carried out as follows:

Eighty-five grms. of the molten fat are mixed, in the case of butter with 40 c.c., or of lard with 60 c.c., of petroleum ether, and for butter 70 c.c., or lard 60 c.c., of N/1 alcoholic potassium hydroxide solution are added; the mixture is shaken for about two minutes and then allowed to stand overnight. One hundred c.c. of 99 per cent. alcohol are now added, the mixture is transferred to a separating funnel, 200 c.c. of water are added, and the whole is mixed, but must not be shaken violently. The turbid aqueous layer is then run off, and the petroleum spirit layer, which is also turbid, is gently shaken with 45 c.c. of 99 per cent. alcohol and 55 c.c. of water; the aqueous layer is again drawn off, and the petroleum ether layer is then shaken violently with 45 c.c. of 99 per cent. alcohol and 55 c.c. of water. The petroleum ether now separates as a clear layer, which is drawn off and evaporated on the water-bath. The residue of esters thus obtained is then submitted to distillation; for this purpose 50 grms. of the esters are introduced into a distillation-flask, the bulb of which has a capacity of 110 c.c.; the neck of the flask is 16 mm. in diameter, and the side-tube, which has a diameter of 5 mm., is fitted on the neck at a height of 9 cm. from the bulb. After the addition of 1 c.c. of ether and a small quantity of powdered pumice-stone, the contents of the flask are heated by means of a burner so placed that the flame does not touch the gauze on which the flask rests. A thermometer is fitted in the neck of the flask in such a manner that the upper part of the bulb is level with the lower edge of the side-tube of the flask. At first ether and

traces of water distil over, and when the temperature rises to 190°, the distillate is collected in a tube graduated in tenths of a c.c. The distillation of the ester commences at 230° to 240°, and when the temperature rises to between 299° and 300° the flame is removed from under the flask, the temperature is allowed to sink to about 270°, and once more raised to 300°. The volume of the distillate is now observed. In the case of pure butters it varies from 2·5 to 6·1; for coconut oil it lies between 40·0 and 42·0, and for lard between 0·5 and 1·1 c.c.

It has been shown by A. Hepner (*J.S.C.I.*, 1911, 30, 974) that cows fed on beetroot leaves yield butter giving an abnormally high value by this method. (Cf. Polenske, *J.S.C.I.*, 1912, 31, 147.)

The Kirschner Method

This method (*Analyst*, 1905, 30, 205) depends upon the solubility of silver butyrate in dilute silver nitrate solutions, whilst the silver salts of the higher fatty acids are practically insoluble. Revis and Bolton (*Analyst*, 1911, 36, 333), who were instrumental in introducing the process into this country, proceed as follows:

To the 100 c.c. of the 110 c.c. distilled and titrated with baryta in the Reichert-Polenske process (care having been taken not to exceed the neutral point) is added 0·5 grm. of finely powdered silver sulphate, and the whole allowed to stand for an hour, with occasional shaking. The liquid is then filtered, 100 c.c. measured off, 35 c.c. of water and 10 c.c. of sulphuric acid (as previously employed) added, together with a long piece of aluminium wire, and 110 c.c. again distilled off in the standard Reichert-Polenske apparatus in twenty minutes; 100 c.c. are titrated, and the number of c.c. so obtained corrected for the blank is calculated to the Kirschner value by the following formula:

$$K = x \times \frac{121 \times (100 + y)}{10{,}000};$$

where x = the corrected Kirschner titration;

y = the number of c.c. of baryta used to neutralise 100 c.c. of the Reichert-Meissl distillate.

The figure obtained is practically a measure of the butyric acid present and is almost solely used in the determination of butter fat in margarine and other mixtures. The relationship of this figure to the Reichert and Polenske figures is discussed under butter on page 389.

A similar method which is not so useful is that described by Jensen (*Analyst*, 1905, 30, 398) as the "Caprylic acid value." The method depends upon the fact that caprylic acid, when mixed with myristic, palmitic and oleic acids is practically insoluble in water, whilst being volatile in steam. R. K. Dons (*Analyst*, 1907, 32, 383; 1908, 33, 122) carries out the process as follows:

Five grms. of the fat are saponified in the usual way; the soap is dissolved in 100 c.c. of hot water, and decomposed by the addition of 50 c.c. of dilute sulphuric acid. The mixture is placed aside until the fatty acids have solidified, and the clear aqueous portion is drawn off. The cake of fatty acids is now shaken twice with 150 c.c. of water at a temperature of 80° and the aqueous extracts are removed. The insoluble fatty acids are then placed in a flask; 150 c.c. of water, 20 grms. of glycerol, 5 grms. of sodium

sulphate, and a few pieces of pumice-stone are added and the whole is distilled until 110 c.c. of distillate have been collected. The addition of the glycerol and sodium sulphate makes the conditions of the distillation the same as in the ordinary Reichert-Meissl distillation. The distillate is filtered, 100 c.c. of the filtrate are neutralised as usual, and the caprylic acid value of the neutral solution is estimated by precipitating the fatty acids in the neutralised Reichert-Meissl distillate with N/10 silver nitrate solution and calculating the volume of silver used into c.c. of N/10 caprylic acid per 5 grms. of the fat. A correction is applied for the solubility of the silver salt in the volume of solution, and wash water used—namely, 0·4 c.c.—which is added to the value obtained. Under these conditions pure butter fat gives a value of from 1·6 to 2·0; butter fat mixed with 10 per cent. of coconut oil 2·6 to 3·0; and pure coconut oil 5·3.

A similar method has been suggested by Wijsman and Reijst (*Analyst*, 1906, 31, 158), which has been discussed, somewhat unfavourably, by F. Jean (*Analyst*, 1906, 31, 260), Morgenstern and Wolbring (*Analyst*, 1907, 32, 118) and C. Barthel (*Analyst*, 1908, 33, 236).

The Modified Method of Monhaupt.—M. Monhaupt (*Analyst*, 1909, 34, 212) has suggested a modified method for the Reichert-Kirschner value, which appears to have points of value particularly for the detection of very small quantities of butter fat. The method is carried out as follows :

Five grms. of the sample are saponified as usual with sodium hydroxide in glycerol solution, and the soap is dissolved in 90 c.c. of water; 50 c.c. of dilute sulphuric acid are added, and the mixture is heated for some time until the liberated fatty acids form a clear layer. After cooling, the aqueous portion is passed through a dry filter, and the clear filtrate is distilled, a little pumice-stone being added to the flask, until 110 c.c. of distillate have been collected. This distillate is filtered, and 100 c.c. of the filtrate are titrated with N/10 alkali solution as usual. The number of c.c. of the alkali required multiplied by 1·1 gives the " new " Reichert-Meissl value of the fat. The neutralised distillate is then treated with silver sulphate, etc., as described by Kirschner (*loc. cit.*). The result obtained is termed the " new " Kirschner value. The influence of from 1 to 2 per cent. of butter fat in a margarine containing from 15 to 35 per cent. of coconut oil is seen from the following results (cf. Gilmour, *Analyst*, 1925, 50, 272) :

TABLE XLIV.—TABLE OF NEW KIRSCHNER VALUES

Percentage of Coconut Oil.	Percentage of Butter Fat.	New Reichert-Meissl Value.	New Kirschner Value.
15	0	0·50	0·24
	1	0·72	0·39
	2	0·99	0·62
25	0	0·88	0·30
	1	0·99	0·55
	2	1·21	0·69
35	0	1·10	0·36
	1	1·32	0·63
	2	1·50	0·81

The Modified Method of Blichfeldt.—This process (*J.S.C.I.*, 1910, 29, 792) is similar to the Kirschner process in principle, but it has the disadvantage of requiring a special form of apparatus. It has, however, been largely used in margarine works in this country and a large number of results have been obtained by its means, so that a description must be given here although it has not come into general use, neither does it offer any advantages over the Polenske method. The modified process is described by Blichfeldt (*J.S.C.I.*, 1919, 38, 150T) in the following way :—

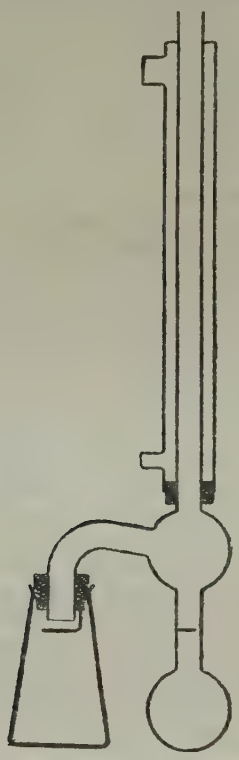

FIG. 5.—Blichfeldt Apparatus

[From the *Journal of the Society of Chemical Industry*

Special solutions required :

(*a*) Caustic potash, made by dissolving potassium hydroxide in an equal weight of distilled water.

(*b*) Sulphuric acid containing 12½ grms. of concentrated acid per litre.

(*c*) Iron alum indicator, made by adding to a saturated solution of iron alum half its volume of nitric acid (one part of concentrated acid to three parts of distilled water).

20 grms. of the filtered fat is weighed accurately into a 300 c.c. resistance conical flask, and 8 c.c. of potash solution (*a*) 25 c.c. of glycerol, and a few small pieces of broken porous tile are introduced. The mixture is cautiously heated over a naked flame, with constant shaking until saponification sets in, care being taken to avoid overheating.

The product, which should be straw-yellow in colour, is cooled and is then made up to 200 c.c. with distilled water which has been boiled for some time to free it from carbon dioxide.

50 c.c. of this soap solution, corresponding to 5 grms. of the original fat, is measured into a 300 c.c. resistance conical flask, 100 c.c. of sulphuric acid solution (*b*) added, and 0·1 grm. of pumice powder sifted into it through butter muslin.

The flask is now connected to the apparatus, and the requisite quantity, indicated by the mark between the two bulbs, is distilled over in about twenty minutes. As soon as the distillation is finished, the flask and condenser jacket are removed, and the side tube is closed by a cork. 0·5 c.c. of a 1 per cent. phenolphthalein solution and a known excess of from 5 to 10 c.c. of N/10 sodium hydroxide solution is now introduced through the condenser tube, which is then closed with a cork. The volatile acids are completely dissolved in the hot alkali solution by shaking; at the beginning of the shaking operation, the cork is withdrawn once or twice to lower the pressure inside. The resulting solution of sodium salts of the volatile acids is transferred to a 200 c.c. measuring flask, and the condenser tube is rinsed out several times with warm water into the flask. The volatile acids are then determined in the cool liquid by difference by titrating the excess of alkali with N/10 sulphuric acid solution, a deduction of 0·4 c.c. for a blank experiment being made.

The insoluble silver salts are now precipitated from this neutral liquid by adding N/10 silver nitrate solution (5 c.c. in excess of the number of c.c. of N/10 sodium hydroxide required to neutralise the volatile acids), and

complete precipitation of the insoluble silver salts from the solution is effected by dissolving in it 20 grms. of pure sodium nitrate. The liquid is then made up to 200 c.c., repeatedly shaken for about five minutes, and 175 c.c. filtered into a measuring flask. The filtrate is transferred to a 300 c.c. conical flask, and, after adding 15 c.c. of the iron alum indicator (*c*), titrated with N/10 potassium thiocyanate solution until a red colouration just appears. The number of c.c. of thiocyanate solution required $\times 8/7$, subtracted from the number of c.c. of silver nitrate solution used gives the equivalent of the soluble silver salts.

The complete apparatus is obtainable from Messrs F. E. Becker & Co., Hatton Wall, London, E.C. The mark between the two bulbs indicates 100 grms. of water at 65°. It is advisable to test the accuracy of the mark by filling the bulb with 100 grms. of water and placing it in a water-bath at 65°.

The following figures have been obtained by various workers using this method:

TABLE XLV.—RESULTS FROM MODIFIED BLICHFELDT METHOD

Fat.	Total Volatile Acids Range.	Total Volatile Acids. Average.	Insoluble Range.	Insoluble Average.	Soluble Range.	Soluble Average.	M.Pt. Insoluble Volatile Acids.
Coconut .	19·3–23·1	21·0	16·3–19·7	18·0	2·6–4·3	3·0	7·8–12·5
Palm-kernel .	12·6–15·4	13·5	9·4–12·9	11·0	2·0–3·5	2·5	21·0–24·5
Butter .	26·4–33·9	32·0	4·0–6·5	4·0	22·2–27·5	28·0	..
Oleo products	..	..	0·4–0·7	..	..	..	..
Coconut stearine .	10·3–20·5	..	9·5–19·0	..	0·6–2·4	..	26·4–32·0

A simpler method has been suggested, by Elsdon (*Analyst*, 1925, 50, 61) which is carried out in the following way:

35 c.c. of N/10 $AgNO_3$ are added to the neutralised Reichert distillate, the whole transferred to a 220 flask, diluted to the mark with water and allowed to stand for one hour. After this time 200 c.c. are filtered off and titrated with N/10 ammonium thiocyanate with iron alum indicator. To the number of c.c. used in the titration, one-tenth is added and also the value obtained in a blank experiment (usually about 0·2) and the value so obtained is then subtracted from the original 35 c.c. This figure is then subjected to a further correction of one-tenth, so that it may be compared directly with the Reichert value. This final figure represents the amount of acids present whose silver salts are insoluble under the conditions obtained; the soluble figure is obtained by subtracting this from the Reichert value.

A large number of results obtained by this method are recorded in the above paper, but the figures are not as good as those obtained by the Kirschner process. The figures for small additions of butter fat are not quite so sensitive and, further, there are greater differences between the observed and calculated figures than in the case of those obtained by the Kirschner

process. (Cf. F. H. van der Laan, *J.S.C.I.*, 1923, 42, 287A and M. Zaayer, *ibid.*, 1925, 44, B897.)

Alcohol Solubility (Quantitative) Methods

The first serious attempt to base a method of separation on the solubility of oils in alcohol was that of Vandam (*Analyst*, 1901, 26, 320) whilst a

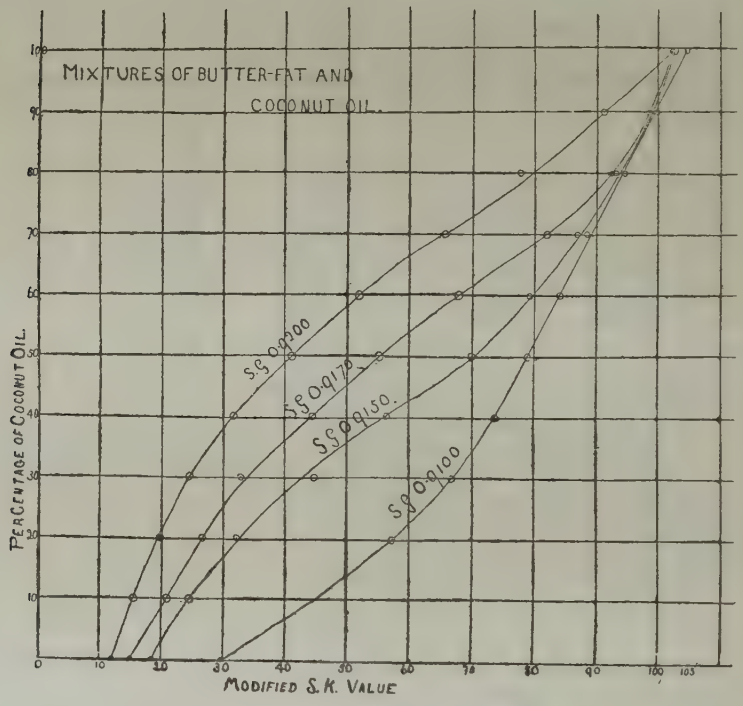

Fig. 6 (*a*).—Shrewsbury and Knapp Method

similar method has been suggested by L. Robin (*Analyst*, 1907, 33, 47; *J.S.C.I.*, 1906, 25, 1055; 1907, 26, 720, 975; 1912, 31, 553). Another method on the same lines was suggested by Fendler (*Analyst*, 1910, 35, 355) who used the residue of insoluble acids left in the distillation flask on the completion of the Reichert-Polenske process. This method has been commented upon unfavourably by A. Hepner (*Analyst*, 1911, 36, 451) and E. Polenske (*Analyst*, 1912, 37, 93) whilst S. H. Trimen (*Analyst*, 1913, 38, 246), though considering the process had possibilities, was not able to give any definite opinion as to its value.

The Shrewsbury and Knapp Process.—A method based upon the same principles, but having a somewhat different technique, was described by Shrewsbury and Knapp (*Analyst*, 1910, 35, 385; 1912, 37, 3). Although

Ross, Race and Maudsley (*Analyst*, 1911, 36, 195) were able to obtain moderately good results by this method subsequent investigators were not able to confirm these. Revis and Bolton (*Analyst*, 1911, 36, 334), S. H. Trimen (*Analyst*, 1913, 38, 245), Elsdon and Bagshawe (*Analyst*, 1917, 42, 72).* Revis and Bolton (*loc. cit.*) suggested an improved method, but this, in an extended trial by Elsdon and Bagshawe (*loc. cit.*), although giving better results, was finally given up as being unsatisfactory. Finally, the

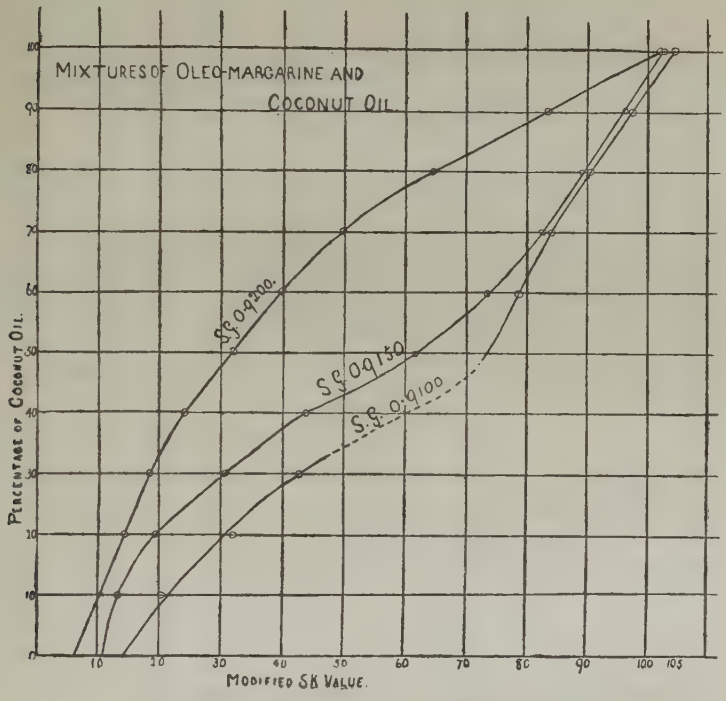

FIG. 6 (*b*).—Shrewsbury and Knapp Method

following method (Elsdon and Bagshawe, *loc. cit.*) was worked out and found to be satisfactory:

5·0 grms. of the fat are weighed out into a 300 c.c. flat-bottomed flask (Reichert flask), and saponified by heating with 15 c.c. of glycerol-soda over a naked flame until the liquid suddenly clears. (The glycerol-soda is made by mixing together 700 c.c. of glycerol and 200 c.c. of a solution of caustic soda made by dissolving 1 pound of " pure by alcohol " caustic soda in 1 litre of water). One hundred and forty-five c.c. of boiling water (measured hot) are then carefully added drop by drop to avoid loss by spurting, and finally 10 c.c. of a 10 per cent. (by volume) solution of sulphuric acid, when the flask is corked and thoroughly shaken. The contents of the

* Cf. Cribb and Richards (*Analyst*, 1911, 36, 327); Macara (*Analyst*, 1911, 36, 341); Cranfield (*Analyst*, 1911, 36, 446).

flask are cooled by immersing the flask in cold water until the fatty acids have set to a compact cake; the liquid is then filtered. Twenty c.c. of boiling water are added to the fatty acids which are retained in the flask, the acids melted, and again cooled. The liquid is poured through the same filter as before, and the cake of fatty acids broken by shaking violently against the sides of the flask, and then transferred to the filter-paper by successive quantities of 20 c.c. and 10 c.c. of cold water. The filter-paper is allowed to drain and then removed from the funnel, it being supported in the rim of

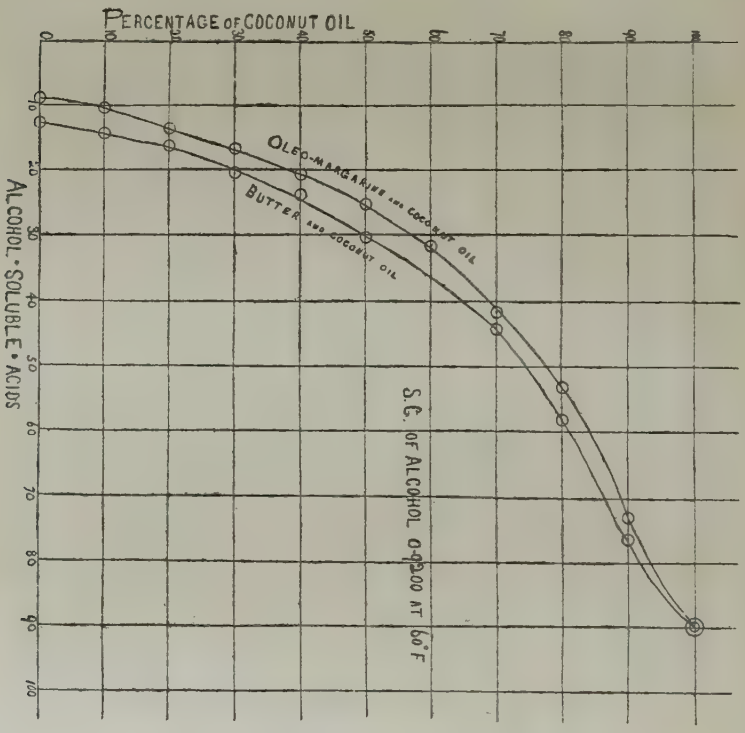
PERCENTAGE OF COCONUT OIL
ALCOHOL-SOLUBLE ACIDS
OLEO-MARGARINE AND COCONUT OIL
BUTTER AND COCONUT OIL
S.G. OF ALCOHOL 0·920 AT 60° F

FIG. 6 (*c*).—Shrewsbury and Knapp Method

the filter stand. The flask is inverted almost, but not quite, vertically over the filter-paper, and the whole is allowed to drain overnight. In the morning the flask is heated in the water-oven for about five minutes, and a current of air is blown through, the filter-paper being then added and the drying continued for a further ten minutes. One hundred c.c. of alcohol (industrial methylated spirit), sp. gr. 0·920 at 15·5°, are next added from a carefully graduated pipette, the flask is corked, and the alcohol heated until the fatty acids have completely dissolved. The alcohol is then cooled below 15·5°, thoroughly shaken, and allowed to stand in water at 15·5° for half an hour or until its temperature is exactly 15·5°. It is then filtered, and 50 c.c. of the filtrate titrated with N/10 caustic soda after the addition of 1 c.c. of 0·2 phenolphthalein solution. In the case of fats containing large quantities of

coconut oil the end-point is rather vague, and a little practice is necessary before it can be judged exactly. No water should be added.

The process is, of course, valuable as a method of detecting the characteristic acids of coconut oil—lauric and myristic, which together form more than 60 per cent. of the oil (*Analyst*, 1913, 38, 8)—instead of those which occur in much smaller quantities and which go to form the Polenske figure. There is also the valuable point that coconut oil and palm-kernel oil give practically identical figures by this method.

The percentage of oil of the coconut group may be calculated from the result obtained by reference to the tables given below, from which a graph may be drawn if desired.

TABLE XLVI.—MIXTURES OF BUTTER AND COCONUT OIL AND OLEO AND COCONUT OIL

Percentage of Coconut Oil.	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
With butter .	12·0	15·6	19·8	24·7	31·7	41·0	52·0	65·8	77·7	91·0	102·0
With oleo margarine .	6·2	10·6	14·4	18·6	24·1	32·2	39·9	49·9	64·6	83·5	102·0

TABLE XLVII.—MIXTURES OF BUTTER, OLEO AND COCONUT OIL

Percentage of Coconut Oil.	Percentage of Butter Fat.				
	0·0.	2·5.	5·0.	10·0.	20·0.
0·0	6·2	6·2	6·3	6·6	6·9
5·0	7·6	7·6	7·8	8·0	8·2
10·0	10·6	10·6	10·7	10·8	11·0
20·0	14·4	14·0	14·3	14·8	15·0
40·0	24·1	24·2	24·3	24·7	25·8
60·0	39·9	40·4	40·8	41·8	42·5
70·0	49·9	50·6	52·4	55·3	59·6

The above modification of the Shrewsbury and Knapp value has been combined with the Reichert-Polenske process by Elsdon (*Analyst*, 1917, 42, 295). The results obtained are not quite so good as those obtained by the direct method, but the method has the advantages of convenience and of speed as it is quite possible to perform the combined Reichert-Polenske-Shrewsbury-Knapp process in from two hours to two hours and a half. The method used is as follows:

The flask containing the residual fatty acids after the distillation of 110 c.c. in the Reichert-Polenske process is removed from the condenser, and the contents cooled in water until the acids have become a solid cake. The cake is broken and the liquid strained through a fine wire sieve, the flask and fatty acids being washed with 50 c.c. of cold water. The fatty acids are

allowed to drain on the sieve until practically free from water, when they are returned to the flask, the last portions being removed with a thin iron spatula; no difficulty has been experienced in removing the last traces in this way. The flask and contents are then dried in the oven, air being blown through the flask at intervals. One hundred c.c. of alcohol (sp. gr. 0·9200 at 15·5° from industrial methylated spirit) are then added, and the process continued from this point exactly as is given above.

The following results are obtained using the mixtures indicated, from which it will be possible to calculate the composition of other mixtures which are examined:

Table XLVIII.—Mixtures of Coconut Oil with Butter and with Margarine

(Sp. Gr. of Alcohol 0·9200 at 15·5)

Percentage of Coconut Oil.	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
With butter .	12·7	14·5	16·5	20·6	24·0	30·4	..	44·4	58·3	76·5	89·8
With oleo-margarine .	8·9	10·6	13·7	16·9	20·8	25·4	31·8	41·8	53·4	73·2	89·8

The Avé-Lallement Value

The method of E. Avé-Lallement (*Analyst*, 1907, 32, 382) is based upon that of König and Hart (*Analyst*, 1891, 16, 139). It depends upon the respective solubilities of the barium salts of the fatty acids. The process is best carried out in the manner suggested by Revis and Bolton:

Five grms. of the filtered fat are saponified with 50 c.c. of approximately N/2 alcoholic sodium hydroxide (carefully standardised against N/2 HCl), boiling for thirty minutes (see saponification value). While the solution is still warm, it is titrated with N/2 hydrochloric acid to phenolphthalein. The alcohol is then removed as completely as possible by boiling and blowing air into the flask. The soap is dissolved in hot, recently boiled, distilled water, and transferred to a 250 c.c. flask, brought to a temperature of 40°, and made up to the mark at that temperature. 100 c.c. are pipetted off into a flask, which is stood in a boiling water-bath for five minutes, and then 50 c.c. of approximately N/5 barium chloride solution (about 25 grms. of crystallised $BaCl_2 \cdot 2H_{20}$ in 1000 c.c.) are added. The mixture is allowed to remain for fifteen minutes in the water-bath, to cause the insoluble barium salts to coalesce. The contents of the flask are cooled and filtered into a 250 c.c. flask, washing the insoluble soaps well, and making up to the mark. 200 c.c. are pipetted into a beaker, acidified with 1 c.c. of concentrated HCl, heated on a sand-bath nearly to boiling, and 10 c.c. of approximately N/1 sulphuric acid then run in. The beaker is allowed to stand overnight, and the precipitate filtered on a Gooch crucible, and washed till free from chlorides, and finally with two quantities of 10 c.c. of warm alcohol. It is then dried to constant weight. The weight of barium sulphate found is increased by 25 per cent., and calculated to BaO ($BaSO_4 \times 0{\cdot}657$ = barium oxide). This is

subtracted from the barium oxide value of the barium chloride solution (which must be standardised in an exactly similar way). The result is the barium oxide value of the acids forming insoluble salts from 2 grms. of fat, and this, calculated to 1 grm. of the fat = insoluble barium oxide value (*b*). The saponification value, also calculated to barium oxide (KOH × 1·367 = barium oxide) for 1 grm. of fat = total barium oxide value (*a*), and $a-b$ = soluble barium oxide value (*c*), from which is calculated the value of $b-(200+c)$.

The great value suggested for this process is that the figure obtained for $b-(200+c)$ is always negative in the case of butter fat, whilst the addition of either coconut oil or oleo-margarine will produce a positive figure. The following results are given by Avé-Lallement:

TABLE XLIX.—RESULTS OF AVÉ-LALLEMENT METHOD

	R.M. Value.	Mgms. Barium Oxide for 1 grm. of Fat.			
		Total. (*a*).	Insoluble. (*b*.)	Soluble. (*c*).	Difference. $b-(200+c)$.
Butter (fifty samples)—					
Highest	32·3	329·6	254·8	76·7	−23·8
Lowest	24·6	300·9	247·4	50·8	−0·7
Average	28·7	310·7	250·7	60·3	−9·6
Coconut oil (three samples)—					
Highest	9·6	354·1	299·2	57·6	45·1
Lowest	9·0	351·8	296·5	54·1	38·9
Lard (five samples)—					
Highest	..	267·7	259·2	10·4	50·3
Lowest	..	265·0	257·2	7·6	46·9
Sesamé oil	..	255·2	251·9	3·3	48·6
Cotton oil	..	263·5	256·9	6·6	50·3
Butter fat 10 per cent. lard .	26·3	306·7	254·6	52·1	2·5
Butter fat 10 per cent. coconut oil	28·8	318·2	259·2	59·0	0·2
Butter 10 per cent. coconut oil and 10 per cent. beef fat	23·4	311·0	257·2	48·0	3·4

In some cases the difference figure in this column represents an extreme limit, and is not deduced from the analysis of one sample.

Bolton and Revis (Allen, fifth edition, Vol. II) give the following results, but greater difference values (up to −24) were given in the first edition of their *Fatty Foods*. It will be obvious that there is room for a considerable amount of lard in a butter having even a difference value of −13 before suspicion would be aroused as to its authenticity by this test.

It is not for this reason, however, in a worse position than most of the other tests that have been suggested, whilst it should not be forgotten that coconut oil and animal fats, as well as vegetable oils in general, show differences in the same direction. The fact, however, cannot be overlooked that the process needs a large amount of attention, whilst it must be carried through with meticulous attention to detail as two or three milligrams of barium sulphate or 0·1 c.c in the titration make a serious difference to the value of $b-(290+c)$.

TABLE L.—RESULTS OBTAINED BY BOLTON AND REVIS

Butter.	Total Ba.	Insol. Ba.	Soluble Ba.	Difference.	R.M. No.	Polenske No.	Kirschner No.
Danish . .	315·90	252·95	62·95	−10·00	29·7	2·7	24·2
	308·59	251·18	57·41	−6·23	30·6	2·7	23·8
	310·38	253·31	57·07	−3·76	30·2	1·9	23·8
	314·38	254·19	60·19	−6·00	31·8	2·9	22·8
	312·03	254·30	57·73	−3·43	30·1	1·8	21·4
	312·18	252·98	59·20	−6·22	30·4	2·4	21·4
	317·66	256·04	61·62	−5·58	31·8	3·0	20·9
	316·19	254·95	61·24	−6·29	30·9	2·9	..
	317·52	255·90	61·62	−5·72	29·1	3·0	..
	312·78	252·24	60·54	−8·30	31·4	2·3	..
English . .	313·16	253·18	59·98	−6·80	30·1	2·3	24·6
	312·71	252·98	59·73	−6·75	29·8	2·4	21·9
	312·04	253·57	58·47	−4·90	30·1	2·5	21·9
	314·38	255·35	59·03	−3·68	28·3	2·1	20·1
	312·26	251·61	60·65	−9·04	31·4	2·4	22·9
	312·88	255·42	57·46	−2·04	29·8	2·4	..
	313·46	254·44	59·02	−4·58	28·5	2·4	..
New Zealand .	309·78	251·40	58·38	−6·98	30·5	2·2	23·1
	316·90	251·86	65·04	−13·18	32·7	2·7	24·7
	311·11	252·03	59·08	−7·05	31·8	2·2	22·0
	317·59	253·87	63·72	−9·85	29·6	3·3	..
	313·41	252·91	60·50	−7·59	32·4	2·7	..
	318·70	254·50	64·30	−9·70	32·2	3·0	..
	316·25	254·15	62·10	−7·95	32·4	2·6	..
Irish . . .	315·83	256·23	59·60	−3·37	32·2	2·8	..
	314·68	254·03	60·65	−6·62	31·4	2·5	..
	311·41	254·24	57·17	−2·93	28·1	2·1	..
	309·05	251·55	57·50	−5·95	27·4	2·3	19·2
Normandy .	316·43	253·90	62·53	−8·63	32·4	3·2	..
	316·26	252·52	63·74	−11·22	31·9	3·0	..
	311·94	254·95	56·99	−2·04	28·8	2·1	..
	316·96	256·73	60·23	−3·50	31·4	2·9	..
Probably adulterated .	312·75	258·17	54·58	−3·59	28·5	2·3	..
	307·22	256·30	50·92	+5·38	26·6	1·8	..
	309·13	257·89	51·24	+6·65	27·1	2·1	..
	303·06	255·48	47·58	+7·90	24·6	1·7	..

Fritzsche (*Analyst*, 1907, 32, 383) confirms the results of Avé-Lallement and the process is very highly spoken of by Bolton and Revis (*Analyst*, 1910, 35, 343; 1911, 36, 392 and *Fatty Foods*) particularly for the examination of Ghee (q.v.). S. H. Trimen, however (*Analyst*, 1913, 38, 243), found

that, although Ghee never gave a positive value for the expression $b-(200+c)$, some of the figures obtained were so low that a negative value is still given after the addition of considerable quantities of coconut oil. Bolton and Revis (*Analyst*, 1915, 40, 501) support their original opinion by stating that their commendation was not directed towards this process as a means of detecting coconut oil but rather to its value for the detection of other animal fats in butter. Supposing that the criticism of Trimen to be correct in regard to the giving of low results for $b-(200+c)$ it follows that considerable additions of oleo margarine would be necessary to convert this into a positive value and thus to prove definite adulteration.

The process is doubtless a valuable one in some cases, but far more results need to be recorded before any definite indications in difficult cases can be accepted.

Some later results by G. Brownlee (*Proc. R. Dublin Soc.*, 1925, 18, 49) on Irish butters do not bear out all the claims that have been made for this process. One hundred and twenty-seven samples of butter were examined and of these twenty gave positive results for the final figure. The negative results varied considerably down to as low as $-21{\cdot}5$, whilst the highest positive result was $+10{\cdot}4$. It is thus seen that in certain classes of Irish butter, at least, the method may be no more reliable than the more usual methods.

The Cadmium Method.—This method, which was suggested by Paal and Amberger (*Analyst*, 1909, 34, 99), is carried out in a special apparatus although doubtless similar results might be obtained in the standard Polenske still. The distillate is precipitated by means of a solution of cadmium sulphate and the weight of this determined after filtering in a Gooch crucible and drying. Using the method of the originators of the process butter fat gives figures of 70–90, whilst coconut oil gives 441–470—butter fat obtained from cows on special rations gave, in some cases, however, figures slightly above 100. By taking into account the saponification value and the " difference value " proposed by Juckenack and Pasternack (*Analyst*, 1904, 29, 156) in conjunction with the cadmium value, it is still possible to detect the presence of added coconut oil in butter, and the authors consider that a butter is adulterated with this oil if (1) the cadmium value is over 100 and the difference value lies between $4{\cdot}25$ and $-3{\cdot}5$; (2) the cadmium value exceeds 110, the saponification not higher than 235, and the difference value at the most -8; (3) the cadmium value is 120, but the saponification value not higher than 235, and the difference value more than -8; (4) the saponification value is over 235, and the cadmium value over 230.

This method has not been used to any extent neither is it likely, at any rate in its present form, to supersede those more generally in use. Revis and Bolton (*Analyst*, 1911, 36, 334) did a certain amount of work on the process, but it, " on account of its extreme laboriousness and questionable value (in our hands), was soon abandoned."

The Magnesium Salt Method.—This method, proposed by E. Ewers (*Analyst*, 1910, 35, 353), depends on the different solubility of the magnesium salts of the fatty acids obtained from the fats, and, further, on the varying solubility of the fatty acids from the soluble magnesium salts in petroleum spirit. Five grms. of the fat are saponified with alcoholic potassium hydroxide solution, the mixture is neutralised with N/2 sulphuric acid, the alcohol is removed by evaporation, and the soaps are dissolved in hot water. The solution is transferred to a 250 c.c. flask, and, after cooling, 50 c.c. of N/2 magnesium sulphate solution are added, and the mixture is diluted to the mark. The contents of the flask are now mixed thoroughly, filtered,

and 200 c.c. of the filtrate are treated in a separating funnel with 10 c.c. of N/2 sulphuric acid, and shaken out with three successive quantities of 50 c.c. of petroleum spirit. The petroleum spirit extracts are washed with several quantities of water (40 c.c., 40 c.c., and 20 c.c.), and the acid aqueous solution, together with the washings (measuring 310 c.c. in all), is distilled after the addition of 1 c.c. of dilute sulphuric acid (1 : 3) and a little pumice-stone. Two hundred and fifty c.c. of distillate are collected and titrated with N/10 alkali solution, using phenolphthalein as indicator; the number of c.c. of N/10 alkali required gives the " distillate magnesium number " of the fat—that is, the quantity of alkali required to neutralise the fatty acids from the soluble magnesium salts which remain in the aqueous solution after treatment with petroleum spirit; this number is expressed per 4 grms. of the original fat. The petroleum spirit solution is now placed in a separating funnel containing a quantity of alcohol and a little phenolphthalein solution; N/10 alkali solution is then run in until the solution remains deep red in colour after vigorous shaking, and the excess of alkali is next titrated back with N/10 acid. The number of c.c. of N/10 alkali used for the neutralisation in this case is termed the " petroleum spirit magnesium number " of the fat, and is a measure of that portion of the fatty acids from the soluble magnesium salts which can be extracted from their aqueous solution by petroleum spirit. The two above-mentioned " numbers " added together give the " total magnesium number " of the fat. On subtracting the " petroleum magnesium number " from the " distillate magnesium number," a " difference figure " is obtained which has a distinctly different value for various fats. The following " numbers " were found on the analysis of a number of samples of fats:

TABLE LI.—RESULTS FROM MAGNESIUM SALT METHOD

	R.M. Number. (5 grms. Fat.)	Total Magnesium Number.	Distillate Magnesium Number.	Petroleum Spirit Magnesium Number.	Difference Number.
		c.c. N/10 Alkali per grms. Fat.			
Butter (19 samples)—					
Minimum	27·7	25·5	17·8	7·7	+10·1
Maximum	30·4	30·4	20·8	10·1	+11·9
Coconut oil (4 samples)—					
Minimum	6·4	26·7	1·3	25·3	−23·9
Maximum	6·7	27·2	1·4	25·9	−24·5
Lard (8 samples)—					
Minimum	..	0·0	0·0	0·0	0·0
Maximum	..	0·4	0·3	0·1	+0·2

Ewers claims that the presence of 10 per cent. of coconut oil in butter fat is plainly indicated by a decrease in the " distillate magnesium number," an increase in the " petroleum spirit magnesium number," and an increase in the " difference number "; with this proportion of coconut oil the latter value lies between 6·5 and 8·3. A determination of the " petroleum spirit magnesium number " affords a means of detecting as little as 5 per cent. of coconut oil in lard. It is also possible to detect the presence of about 15 per cent. of lard in butter by means of the above-mentioned method.

This method has been examined by C. Amberger (*Analyst*, 1911, 36, 404), E. Nockmann (*Analyst*, 1911, 36, 451), and E. Polenske (*Analyst*, 1912, 37, 93), all of whom make unfavourable criticisms. It was found that cows at the end of their lactation periods give butter fat having a Reichert value of 18·1–21·7 also gave abnormally low results by this process, whilst the same results were obtained by feeding the cows on coconut cake or beetroot leaves. In its present form the method cannot, therefore, be recommended, but in view of the possibilities of the barium method of Avé-Lallement, the study of various modifications might repay the trouble involved.

The Method Recommended.—In the present state of our knowledge concerning the composition of those fats containing volatile fatty acids the best process to adopt is undoubtedly the standard Reichert-Polenske-Kirschner process described on page 148. For special purposes described under the appropriate heading the Shrewsbury and Knapp value will be found of distinct utility. Of the other processes those of Avé-Lallement and Monhaupt, particularly that of the former, show promise, but at present they will only be of value to those having had considerable experience of them.

CHAPTER X

DRYING OILS *

Candle-Nut Oil

Source.—Candle-nut oil is obtained from the kernels of the fruit of a species of *Aleurites*. The earlier writers gave this as *A. moluccana* (or *molucana*) but this is stated (*J.S.C.I.*, 1914, 33, 837) to be little, if any, different from *A. triloba*, and the oils are very similar if not identical. *A. moluccana* is found in several Oceanic islands and also in parts of the West Indies, in Brazil, in Florida and in Hawaii. (A similar nut, mistaken at first for candle nut, is mentioned in literature (*J.S.C.I.*, 1914, 33, 556) but the oil was non-drying and was obviously from a different source.) The oil is variously known as Kukui, kekune, walnut and artists' oil. The fruit (known as Kukui nuts) resemble walnuts, but have a thicker shell. There is some confusion as to the possibility of using the oil as an edible oil after suitable purification for, although the seeds contain a violent purgative it is said to remain almost entirely in the press-cake. (Lespinasse, *Analyst*, 1919, 44, 343.) The seeds consist of about one-third kernels which contain 60–70 per cent. of oil.

Composition and Properties.—The oil contains oleic, linolic, linolenic, stearic, palmitic and myristic acids. West and Montes (*Analyst*, 1922, 47, 27) state that the fatty acids consist of 6·5 per cent. of linolenic acid, 33·5 of linolic, 57·0 of oleic and 2·8 of solid acids. The oil has excellent drying properties and was found by Walker and Warburton (*Analyst*, 1902, 27, 237) to yield about 8 per cent. of insoluble bromides.

The following results have been obtained in the examination of the

Table LII.—Examination of Candle-Nut Oil from *Aleurites Moluccana*

Observer.	S. G. 15·5°	Sap. Val.	Iodine Value.	40° *n*	Acid Val.	Titre. °C.	M.Pt. of Acids. °C.	R.M.	Sol. Pt. °C.
J.S.C.I., 1914, 33, 1018	0·928	188	151·6	1·4716	0·8				
Gardner	0·927	192	162	1·4711	1·3				
West and Montes . .	0·921†	214	140‡						
Imperial Institute . .	0·927	194	151						
Lewkowitsch . . .	0·926	193	164	1·4706		13	20–21		
Fendler §	0·925	195	114			15·5	18	1·2	−15

* This classification is adopted merely for convenience—the three classes, drying, semi-drying and non-drying are not always sharply distinguished.

† At 31°/4°. ‡ Hübl.

§ From *A. moluccana* obtained from Cameroons by extraction with ether; oxidation had probably taken place as the other figures are mostly obtained on expressed oils. An oil of I.V. 118 was obtained by Lach but in this case the titre was 56. Undoubtedly some confusion has arisen.

oil from *A. moluccana* by different observers. The results from *A. triloba* are placed in a separate table below. The oil from *A. moluccana* is also described as lumbang oil by some writers. For the oxidation and hydrogenation of the oil see West, Gonzaga and de Leon (*Analyst*, 1924, 49, 38, 246).

The tree *A. triloba*, which is common in Hong-Kong, yields the nuts which are known as kirimi nuts, and which in turn yield the oil known in India as kekuna oil. As already mentioned above the tree is similar to, if not identical with, *A. moluccana*. Constants for the oil are given below.

For the constants of walnut oil cf. page 186, and *J.S.C.I.*, 1913, 32, 496; 1923, 42, 276A.

TABLE LIII.—EXAMINATION OF CANDLE-NUT OIL FROM *Aleurites Triloba*

Observer.	S.G. 15·5°.	Sap. Value.	Iodine Value.	Acid Value.	R.M.	Titre. °C.
Lespinasse	0·927	175	137	1·4		
Imperial Institute . . .	0·927	194–204	140–151		2·0	17·8

Soft lumbang oil is obtained from *Aleurites trisperma* (cf. *J.S.C.I.*, 1919, 38, 952A), and is somewhat similar to candle-nut oil in iodine value and drying power. The plant is cultivated to some extent in the Philippine Islands. The yield of oil is about 30 per cent. on the unshelled nuts or 50 per cent. on the kernels. The oil slowly polymerises on exposure to light giving a granular mass resembling the product from tung oil (*A. fordii*). The following constants have been recorded by Aguilar (*J.S.C.I.*, 1918, 37, 215A) and by Gardner (*J.S.C.I.*, 1919, 38, 952):

TABLE LIV.—EXAMINATION OF CANDLE-NUT OIL FROM *Aleurites Trisperma*

Observer.	S.G. 15°.	Sap. Value.	Acid Value.	Iodine Value.	n 40.
Aguilar	0·937	197·7	8·7	145	
Gardner	0·938	194	4·4	164	1·4876
Gardner	0·938	190	7·1	161	1·4873

The oil from *Aleurites montana*, Wilson, which occurs in India has been examined by Parker and his collaborators (*J.S.C.I.*, 1924, 43, 478B), who found the principle fatty acid present in the oil to be β-alæostearic acid (M.Pt. 73°). The other liquid acids present were oleic and linolic. The following constants were observed:

Specific gravity 15°	0·947
Refractive index 40°	1·4815
Acid value	3·5
Saponification value	203
Iodine value	141
Unsaponifiable matter per cent. . . .	0·6
Titre °C.	54

Kaya Oil

Kaya oil is obtained from the seeds of *Torreya nucifera*, S. et Z., a plant which grows wild in the mountainous districts of Japan. The kernels contain 48 to 52 per cent. of a pale yellow oil suitable for edible purposes which may be obtained by expression. Ueno (*Analyst*, 1913, 38, 458) states that the fatty acids consist of about 9 per cent. of palmitic and stearic acids, 19 per cent. of oleic acid and 72 per cent. of a linolic acid which yields a sativic acid melting at 151° to 152° instead of the usual 174°. Tsujimoto (*Analyst*, 1908, 33, 238) states that the oil does not become turbid at −20°, that it yields an elastic film when heated for three hours at 100° and dries at the ordinary temperature after boiling with manganese resinate, and that the fatty acids yield a tetrabromide but give no deposit in the insoluble bromide test on the oil. The figures obtained by Tsujimoto together with those of Higuchi (*J.S.C.I.*, 1916, 35, 262) are here given:

Table LV.—Examination of Kaya Oil (Tsujimoto and Higuchi)

Constant.	Tsujimoto.			Higuchi.
	1.	2.	3.	
Specific gravity 15°	0·924	0·923	0·924	0·924
Acid value	1·5	4·2	12·7	0·48
Saponification value	188·4	188·3	188·0	190·1
Iodine value	142·2	138·0	133·0	135·8
Reichert-Meissl value	0·9	..	..	0·7
Refractive index 40°	1·4697	1·4687	1·4684	..

Lallemantia Oil

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, a plant which grows wild in South-East Europe and Central Asia, and which is cultivated to some slight extent. The oil, which resembles linseed oil, is used in Persia and neighbouring countries to some extent as an edible oil and for other purposes. The oil has not been examined to any great extent, but the following results are quoted by Lewkowitsch:

Specific gravity 20°	0·934
Solidifying-point °C.	−35
Saponification value	185
Iodine value	162
Reichert value	1·6
Titre °C.	11
Melting-point of fatty acids	22

Linseed Oil

Source.—Linseed oil is obtained from the seeds of the flax plant *Linum usitatissimum* L., which is specially cultivated for oil-bearing purposes in Russia, India, North and South America, etc. The oil is commercially one of the most important, but as it is mostly used for industrial purposes and only to some slight extent, notably in Russia, for edible purposes, an

amount of space cannot be allotted to it commensurate with its commercial importance.

The characters of the oil depend to a considerable extent upon the source of the seed from which the oil is pressed, both on account of the actual variation in the seed itself and also because of the admixture with foreign seeds to which consignments from some districts are particularly liable. Before passing a definite opinion, therefore, on the purity of a linseed oil it is desirable, if possible, to obtain some knowledge of the alleged source of the oil, although, unfortunately, this is not often possible. The Baltic and Canadian oils are usually the best, Indian good and closely approximating at times to Baltic oil and then Black Sea, Plate River and North American oils in this order of value.

Edible linseed oil is obtained by pressure in the cold when the oil obtained has a characteristic though not altogether unpleasant flavour. The commercial oils being usually hot expressed have a somewhat harsh bitter taste and are not suitable, therefore, for use for edible purposes. Attempts were made a few years ago to produce a tasteless edible oil from linseed oil with a fair amount of success, but there is not much demand as it cannot be used for cooking or frying. An account of this type of work is given in the *Report of the Food Investigation Board for* 1919 (London : H.M. Stationery Office) on page 27.

Some samples of linseed and linseed cake contain substances which yield hydrocyanic acid under suitable conditions, this subject has been studied in detail by Collins and Blair (*Analyst*, 1914, 39, 70; 1915, 40, 125), whose work should be consulted for full particulars on this point. (Cf. H. T. Cranfield, *Analyst*, 1925, 50, 18.)

The seed contains from 35–40 per cent. of oil, the amount depending upon the source and varying to a certain extent from year to year. Sheppard has given the following figures for seeds of different origins, the amount of oil being that contained in the pure picked seed :

TABLE LVI.—ANALYSIS OF LINSEED OIL SEEDS (SHEPPARD)

Source of Seed.	Per cent. of Oil in Pure Seed.	Oil of one Seed in Milligrams.	Per cent. Oily Impurities.	Per cent. Non-oily Impurities.
America	39·7	4·6	1·5	1·7
America	39·4	4·5	1·0	1·1
La Plata	37·0	5·6	0·6	5·6
Calcutta	40·8	5·4	4·9	5·0
Bombay	41·2	7·9	0·8	2·8
S. Russia (Keotch) . . .	39·1	5·7	5·1	1·7
N. Russia (Riga) . . .	37·0	4·2	3·3	2·0

Properties.—Linseed oil is the typical drying oil, the best Baltic oil being used almost as a standard by which the drying power of other oils is judged. When thin films of the oil are exposed on glass plates, drying is very rapid and its rate of drying may be further increased by the addition of certain metallic salts known as driers. The dried product is known as linoxyn, its chief characteristic being its insolubility in most organic solvents. It is, however, soluble in glacial acetic acid, in which solvent the iodine value has

been found by Meister (*Analyst*, 1911, 36, 24) to vary from 130 to about 30 according to the length of time the oil had been exposed to the air.

A large amount of work has been done on the properties of linseed oil under various conditions. A discussion of this lies outside the scope of this work, but the following papers may be consulted by those interested in the subject:

"Decomposition of Linseed Oil during Drying." Olsen and Ratner, *J.S.C.I.*, 1912, 31, 937.

"Manganese Content of and Effect of Pigment on Linseed Oil." Boughton, *Analyst*, 1913, 38, 215.

"The Cultivation of Linseed in England." Eyre and Fisher, *J.S.C.I.*, 1915, 34, 559.

"The Formation of Acrolein by the Oxidation of Linseed Oil." Salway, *J.S.C.I.*, 1916, 35, 366.

"Polymerisation of Linseed Oil." Krumbhaar, *J.S.C.I.*, 1916, 35, 1225.

"The Effect of Thinners on the Drying of Linseed Oil." Woodmansey, *J.S.C.I.*, 1917, 36, 1253.

"The Effect of Heat and Oxidation on Linseed Oil." Friend, *J.C.S.*, 1917, 111, i. 162.

"Study of the Oxidation of Linseed Oil." Holden and Radcliffe, *J.S.C.I.*, 1918, 37, 429A.

"The Effect of Exposure on Raw Linseed Oil." Sheppard, *Analyst*, 1919, 44, 323.

"The Composition and Constants of Polymerised and Oxidised Linseed Oil." Ingle and Woodmansey, *J.S.C.I.*, 1919, 38, 101T.

"Factors Affecting the Oxygen Absorption of Linseed Oil." De Waele, *J.S.C.I.*, 1920, 39, 48T.

"The Effect of Heating Linseed Oil under Pressure." Coffey, *J.S.C.I.*, 1921, 40, 19T.

"The Cause of Slowness of Drying of Linseed Oil." Eibner, *J.S.C.I.*, 1921, 4P, 551A.

"The Mechanism of the Oxidation of Drying Oils." Coffey, *J.C.S.*, 1921, 119, 1154, 1408.

"The Phenomenon of the Drying of Linseed Oil." Wolff, *J.S.C.I.*, 1921, 40, 706A.

"The Heat Treatment of Linseed Oil." Mabery, *Analyst*, 1923, 48, 459.

"The Polymerisation of Linseed Oil." Friend and Alcock, *J.S.C.I.*, 1924, 43, B525, B754.

"The Effect of Pigments on the Rate of Oxidation of Linseed Oil." Rhodes and Van Wirt, *J.S.C.I.*, 1923, 42, 1233A.

"The Oxidation of Linseed Oil." R. S. Morrell, *Industrial Chemist*, 1925, 1, 68.

"Catalysis of Linseed Oil Oxidation." P. Slansky, *J.S.C.I.*, 1925, 44, B106.

"Iodine Value and Foots Formation of Linseed Oil." G. H. Richard, *J.O.F.I.*, 1925, 2, 57.

"A Contribution to the Chemistry of Drying Oils." G. W. Ellis, *J.S.C.I.*, 1925, 44, 401T, 463T, 469T, 486T, 768B, 930B.

"The Colloid-Chemistry of Linseed Oil." H. Vollmann, *J.S.C.I.*, 1925, 44, B410, B461.

See also *The Chemistry of Drying Oils* by Morrell and Wood. London: Ernest Benn, Ltd., 1925.

Composition.—The composition of linseed oil has been the subject of research by numerous workers such as Mulden, Tolman, Munson, Fahrion, Haller, Hazura and Grussner, but their results have now only qualitative importance. The saturated acids found were myristic, palmitic and stearic, with possibly traces of higher acids, whilst the unsaturated acids consisted of oleic, linolic and linolenic. The quantitative composition has been attacked by several workers in recent years. Morrell (*J.S.C.I.*, 1913, 32, 1091) found that 6 per cent. of saturated acids were present, of which 66 per cent. was stearic and 32 per cent. palmitic. In contradistinction to the work of Haller and others he was unable to detect myristic, arachidic or any other saturated acid. Coffey (*J.C.S.*, 1921, 119, 1414) has calculated the composition of linseed oil from the loss of carbon dioxide and absorption of oxygen during the drying. His results together with those of Friend (*Chemistry of Linseed Oil*, 1917, 56) are given in the following table:

	Coffey.	Friend.
Saturated acids and unsap. .	8·1	10
Glycerol radicle	4·3	4·6
Oleic Acid	5·0	5·0
Linolic Acid	48·5	48·3
Linolenic Acid	34·1	32·1

The oil has recently been examined by Eibner and Schmidinger (*J.S.C.I.*, 1924, 43, B101) who used, however, an oil having an iodine value as low as 173·5. They obtained the following results: α-linolenic acid 20·1 per cent.; isolinolenic acid 2·7 per cent.; α-linolic acid, 17·0 per cent.; β-linolic acid 41·8 per cent.; oleic acid 4·5 per cent.; oxy-acids 0·5 per cent.; glycerol 4·1 per cent.; saturated acids 8·3 per cent.; phytosterol, 1·0 per cent. These results differ considerably from those of earlier observers and it is obviously desirable that further work be done on these lines.

The actual glycerides present have been studied to some extent by Schicht (*J.S.C.I.*, 1915, 34, 1061), who found linolo-palmitostearin and strongly suspected dioleostearin, linolodistearin and oleo-linolopalmitin, but all these glycerides together amounted to scarcely 0·5 per cent. of the oil.

The Examination of Linseed Oil.—Owing to the frequent high price of linseed oil it has been extensively adulterated both with other seed oils when these have been less expensive and also with rosin oil, fish oils and the like—adulteration being particularly rife in the case of boiled oils, the dark colour of which tends to mark the addition of foreign material. The principal tests are the iodine absorption, the drying power and the hexabromide value; they should always be carried out. No linseed oil can be passed as genuine, or at least as satisfactory unless its iodine value is more than 170, and some suspicion must attach to the oil unless this figure is at least 175, and even this figure is low except in the case of a new oil containing a quantity of mucilage; * as has already been stated the iodine values of the best oils approach 190. The other characteristics vary with the iodine value in the case of pure linseed oil so that the experimental figures should be compared for oils having similar iodine values. In the following table a number of figures are given showing how certain other figures vary with the iodine value.

* The oil should always be filtered through a dry filter-paper previous to testing by the iodine value, as even the small amount of water present in the mucilage is sufficient to make the observed iodine value far too low.

TABLE LVII.—EXAMINATION OF LINSEED OILS

Oil No.	Specific Gravity.	Refractive Index n^{40}.	Wijs.	Saponific. Value.	Modified Livache. % gain.	Days.
1	..	1·4742	190	19·4	..	..
2	·935	1·4742	191	19·3	..	..
3	·934	1·4738	189	19·3	15·6	2
4	..	1·4726	177	19·3	..	..
5	·931	1·4723	161	17·7	5·4	1
6	·934	1·4746	194	19·1	17·4	2
7	·932	1·4726	180	19·1	..	..
8	·931	1·4725	181	..	15·0	2
9	·931	1·4725	179	..	14·6	2
10	·936	1·4743	188	..	16·3	2

The following table shows the iodine values of oils from different sources—post-war oils tend to have somewhat lower figures in the Baltic class.

South American *	176–185
Calcutta and Japanese	about 180
Black Sea	176–182
Canadian and N. America	182–186
Baltic	190–204
Chinese	194

The drying power may be tested by one of the quantitative methods given on page 131, when a value varying with the iodine value should be obtained. The following numbers will give some idea of the figures usually obtained. (Liverseege and Elsdon, *J.S.C.I.*, 1912, 31, 207.)

TABLE LVIII.—DRYING POWERS OF RAW AND BOILED LINSEED OIL (LIVERSEEGE AND ELSDON)

Raw Linseed Oil—								
Iodine value	194	188	184	181	180	180	179	176
Percentage gain	17·4	16·3	15·5	15·1	15·2	15·0	14·6	13·8
Boiled Linseed Oil—								
Iodine value	176	171	168	164	163			
Percentage gain	13·9	13·6	14·1	13·5	12·6			

It is very advisable that a simple drying test be carried out in addition. For this purpose perfectly clean sheets of thin glass (cleaned photographic plates serve excellently) are thinly coated with the oil, and then placed on their edge and left exposed to constant conditions alongside other oils similarly treated which are known to be pure. The drying of the sample under

* Grimme (*J.S.C.I.*, 1921, **31**, 782).

examination, and the nature of the film produced should be compared with those of samples of known purity. A pure linseed oil usually dries in less than three days to an elastic skin which is no longer sticky to the touch.

A method which depends upon the insolubility of the dried oil in ether has been devised by Elsdon and Hawley (*Analyst*, 1913, 38, 1) and may be found useful in difficult cases. The interpretation of the results obtained are made in conjunction with the iodine value by means of a curve (cf. page 132).

The Analytical Characteristics.—These are given in the following table, but it must not be overlooked, as already pointed out, that the figures obtained for linseed oil vary with the source of the oil.

TABLE LIX.—ANALYTICAL CHARACTERISTICS OF LINSEED OIL

Observer.	S.G. 15.	Iodine Value.	n_D^{40}.	Sap. Value.	Unsap. %	Acid Value.	Sol. Pt.
Thomson and Dunlop, *A.*, 1906, 31, 282 . .	..	185·5–205·4	1·4735–1·4761	191·4–192·5	0·88–1·25	.. ..	.. ..
Jensen, *A.*, 1911, 36, 407	932	176	1·4730	191·5	0·88	1·3*	..
Standards of Amer. Soc. of testing materials .	0·932 0·936	178 min.	1·4736 1·4751	189–195	1·50 max.	6·00 max.	.. ..
Wolff, *J.S.C.I.*, 1923, 42, 275A	0·930 0·934	170–192	1·4722 1·4742	187–196	.. ..	.. ..	.. ..
B.P.	0·930 0·940	.. 170 at least	1·4725–1·4748	187–195	1·0 max.	3·0 max.	–20 max.
U.S.P.	0·931 0·941	.. 170 at least	.. ..	187 195	.. ..	.. ..	.. ..
Fryer and Weston . .	0·932–0·937	175–200	1·4735–1·4748	189–194	0·5–2·0	10·0 max.	20° (Titre)
Bolton and Revis . .	0·931 0·938	175–200	1·4726–1·4742	189 195	.. 1·3	.. ..	.. ..

Special Tests.—There is no specific test by which linseed oil may be recognised in mixtures with other oils, but there are some tests for adulterants which are valuable and which should be applied to any sample of linseed oil whenever there is any doubt of its purity. A most important test which is especially useful in the detection of fish oils is that in which the insoluble bromides are isolated and examined. The methods for carrying out the test

* River Plate Lab. press.

are fully described on page 129. In the case of a pure linseed oil the amount of insoluble hexabromide obtained under standard conditions is a straight-line function of the iodine value. Where the conditions described by Sutcliffe (*Analyst*, 1914, 39, 28, 388) are followed this relationship is expressed by the equation

$$\text{Per cent. insoluble bromides} = 0{\cdot}63 \times \text{I.V.} - 78{\cdot}0$$

where I.V. is the iodine value of the oil. A deficiency of bromides where the I.V. is over 170 will probably be due to the addition of other drying oils such as tung oil or poppy-seed oil, which give no insoluble bromides. The separated bromides should be white and crumbly and should have M.Pt. 141°–144°. When fish oils are present the bromides darken on heating, owing to decomposition, and have no definite melting-point; in such cases difficulty is usually experienced during filtration. Fish oils may be confirmed by the phytosteryl acetate test. The compound from linseed oil should melt at 128°–129°, but will be lower in the presence of fish oils. (Cf. Thoms, *Analyst*, 1924, 49, 77.)

The oil may also be tested for " break " by heating in a test-tube to over 200° when only a small amount of coagulation should take place. A large break would indicate an immature oil. Another useful test is to shake 10 c.c. of the oil with 10 c.c. of 50 per cent. by volume sulphuric acid in a 25 c.c. stoppered cylinder. The mucilage separates out as a black layer between the acid and the oil and should not occupy more than 0·5 c.c.

Adulteration with rosin oil (which is still practised especially in the case of boiled oils) will be shown by an increase in the unsaponifiable matter (mineral oil will, of course, have the same effect) and may be detected by the application of the Liebermann-Storch test which is described on page 79 and also by smell. Thurston (*J.S.C.I.*, 1914, 33, 556) states that this test will not show a 50 per cent. adulteration with " gloss oil " which is obtained from rosin and that better results are obtained by treating about 5 drops of the oil with 1 drop of concentrated nitric acid when in the presence of *considerable* amounts of " gloss " oil a distinctive reaction will be obtained.

Madia-Seed Oil

Madia-seed oil is obtained from the seeds of *Madia sativa*, which is a native of Chile and California. It is very similar to the sunflower and the seeds and oil have very similar properties to those of the latter. It has been cultivated in Algeria, Asia Minor, Germany and elsewhere, but this cultivation, although not unsuccessful has not been developed. The seeds contain some 30–35 per cent. of a yellowish-brown oil of the semi-drying type although in some of its reactions it resembles the drying oils. The cold-pressed oil has a pleasant odour and taste and is suitable for edible purposes.

The following constants have been observed for specimens of this oil.

Table LX.—Constants of Madia-Seed Oil

Authority.	S.G. 15°.	Sol. Pt. °C.	Sap. Value.	I.V.	Titre. °C.	Unsap. %.
De Negri and Fabris . . .	0·929	−12 to −17	192·8	117·5	20–22	..
	..	..	..	119·5	..	..
Imperial Institute	0·925	..	194·5	128·9	..	0·8

These figures do not agree particularly well, but the differences may be easily accounted for by the former being a cold-pressed oil and the latter an extracted oil.

Manketti Oil

Manketti oil is obtained from the seeds of *Ricinodendron Rautanenii*, a tree growing in various parts of South-West Africa. The seeds weigh about 1·5 grms. each and contain some 60 per cent. of kernels which yield 50–60 per cent. of a light yellow viscous oil having a pleasant odour and taste. The oil has good drying properties absorbing about two-thirds of the amount of oxygen absorbed by linseed oil. The oil gives no insoluble bromides, but the mixed fatty acids yield linolic tetrabromide of M.Pt. 114°. On account of the small proportion of kernels in the fruits (about 10 per cent.) and the difficulty of extraction of the oil therefrom, it is considered by the Imperial Institute (*J.S.C.I.*, 1917, 36, 1018) that the export of the nuts to Europe would not be remunerative. Constants have been determined by Grimme (*Analyst*, 1913, 38, 105), Thoms (*J.S.C.I.*, 1913, 32, 611), Sprinkmeyer and Diedrichs (*ibid.*, 1914, 33, 1097), and the Imperial Institute as set out in the following table:

Table LXI.—Constants of Manketti Oil

Observer.	S.G. 15°.	Sol. Pt.	n^{40}.	Acid Value.	Sap. Value.	R.M.	Pol.	I.V.	Unsap. %	Titre, °C.	M.Pt. Fatty Acids. °C.
Grimme . .	0·929	−8	1·4805*	0·9	194·8	1·2	0·6	134·8	0·85	35	41
Thoms . .	..	−2	..	0·6	195·2	1·1	0·6	130·4	..	..	40
Sprinkmeyer & Diedrichs	0·931	..	1·4807	1·25	193·3	0·8	0·4	128·5	..	35	39
Imperial Institute . .	0·928	..	..	1·9	191·5	..	..	133·6	..	..	..

The oil of the seeds of *Ricinodendron Africanum* has been examined by A. Hébert (*J.S.C.I.*, 1911, 30, 497) and by Pieraerts (*ibid.*, 1918, 37, 430A). The latter author states that the nuts of *Ricinodendron Africanum*, a large tree growing in the French Congo and other countries of West Equatorial Africa, are of about the size of a hazel nut. Unsorted nuts yielded 28 per cent. of kernels, which contained 17·64 per cent. of water and 55·29 per cent. of a pale yellow oil with the following characteristics: Sp. gr. 15/15° C., 0·9345; refractive index at 19·5° C., 1·5028; acid value, 0·86; saponification value, 194·4; Hehner value, 98·85; and M.Pt., 32·3° to 34·5° C. The oil contained 9·77 per cent. of glycerol, and yielded no bromides insoluble in ether.

It is stated to dry more rapidly than linseed oil. Hébert found that the kernels contained 35 per cent. of oil equivalent to 8·7 per cent. from the entire seed, having sp. gr. 0·937, M.Pt., 20°; saponification value, 185; acid value, 16·8; Reichert value, 1·5; iodine value, 87·6; M.Pt. of fatty acids, 43°. The fatty acids consisted of 70 per cent. solid acids and 30 per cent. liquid acids.

* The temperature is given as 15° but if this temperature is correct the refraction would be very different from that found by Sprinkmeyer.

The seeds of *R. Heudolitii* from Southern Nigeria were examined at the Imperial Institute (*Analyst*, 1909, 34, 166). The kernels of the seeds known as " Nsa-sana " seeds, yielded 47·0 per cent. of a pale yellow oil with a taste resembling that of arachis oil. Exposed in a thin layer, it gave a dry film in a few hours, and from practical tests it appeared to stand between linseed and tung oils in its properties. It had the following analytical values : Sp. gr. at 15° C., 0·9347; acid value, 1·2; saponification value, 184·7; iodine value, 148·2; Hehner value, 94·1; Reichert-Meissl value, 1·9; unsaponifiable matter, 1·2 per cent.; and solidification-point of fatty acids, 34·5° C.

The seeds of *R. mahafalense*, as examined by Heim, Garrige and Husson (*J.S.C.I.*, 1921, 40, 664A), yield 81·4 per cent. of kernels containing 58 per cent. of oil. The cake from the undecorticated nuts is poisonous. The oil is of a pale golden-yellow colour, is semi-drying, and consists entirely of glycerol, of stearic, and oleic acids with a small quantity of triglycerides of volatile fatty acids and hydroxy acids.

N'Gart Oil

This oil is obtained from the kernels of the fruit of *Plukenetia conophora*, a climbing plant cultivated by the natives of the Cameroons, and by them used as an edible oil. The oil is similar in its properties to linseed oil, and as the quantities available are by no means negligible, its use as a substitute for the latter is by no means unlikely.

The fruit, which is about the size of a walnut, consists of about one-third shell and two-thirds kernel, the latter containing 50–60 per cent. of oil of which about 35 per cent. can be obtained by expression. The oil was found by Mühle and Hammelmann (*J.S.C.I.*, 1913, 32, 874) to yield 47·7 per cent. of insoluble bromides which had M.Pt. 177°–178°. The following results have been obtained from an examination of this oil by various observers.

Table LXII.—Constants of N'Gart Oil

Observer.	S.G. 15°/15°.	Sap. Value.	I.R. 40.	I.V.	Acid Val.	Unsap. per cent.	Titre.	Sol. Pt.
Krause . . .	0·936	190	1·4744	204	..	..	..	..
Mühle and Hammelmann . .	0·939	191·7	1·4753	198·3	34·3	0·21	24–25	..
Lewkowitsch* .	0·936	192	..	177–204	..	..	..	−16 to −20

Niger-Seed Oil

Niger-seed oil is obtained from the seeds of *Guizotia abyssinia*, which is indigenous to Abyssinia and which is largely grown there and in other parts of East Africa for local use, and on a large scale in India. The seeds (which are, botanically speaking, achenes) contain some 40 to 50 per cent. of oil, and are small and glistening black in colour.

* Cf. *J.S.C.I.*, 1912, 31, 545.

The cold-pressed oil is the only one used for edible purposes. It is largely used in this way, especially in India, and of recent years quantities of the oil have been used in margarine manufacture in this country. The edible varieties are of a golden-yellow colour with only slight odour and a pleasant nutty flavour. The oil has been stated by various observers to be a good drying oil, but Utz (*Analyst*, 1911, 36, 358) states that it dries very slowly even at 100° but that the speed of drying is accelerated by " boiling." The oil is stated by Mitchell (*Oils, Fats, Waxes, etc.*, London, 1921) and by Vuaflart (*J.S.C.I.*, 1911, 30, 965) to give practically no precipitate in the insoluble bromide test, but Vuaflart states that it gives the arachidic acid reaction. This last statement is in need of confirmation on account of the possibility of confusion with arachis oil and also as it would be a useful test. No other specific tests for the oil have been suggested. Vuaflart states that practically the only difference between niger-seed oil and poppy-seed oil is in their solidification points.

The characteristics of the oil have been determined by various workers as set out in the table below :

TABLE LXIII.—CHARACTERISTICS OF NIGER-SEED OIL

Observer.	S.G. 15°.	Sap. Value.	[3] Iod. Value.	Sol. Pt. °C.	n_D^{40}.	Reichert.	M.Pt. Fatty Acids. °C.	Acid Value.	Unsap. %.
[1] Mitchell . .	0·927	191·7	126·4	−8	..	..	..	..	..
[2] Crossley and Le Sueur . .	0·925–0·926	188·9–192·2	126·6–133·8	..	1·4678–1·4689	0·1–0·6	..	5·2–11·7	..
Utz (Crude .	0·925	123·5	126·8	..	1·4677	0·9	28·2	3·70	1·26
Utz (Bleached .	0·925	217·8	114·0	..	1·4673	3·9	27·8	0·45	0·53
Vuaflart . . .	0·923	..	128·5	−6	1·4676	..	..	..	..
Imperial Institute	0·925	189–192	127–134	..	..	..	..	..	..

[1] *Oils, Fats and Waxes, etc.*, London, 1921, page 568. Oil extracted with ether. [2] *J.S.C.I.*, 1898, 17, 992. Values for four Indian Oils. [3] Archbutt found 132·9 on one sample.

PERILLA OIL

Source.—Perilla oil is obtained from the seeds of *Perilla ocymoides* L., which grows in China and Japan and has been cultivated there and in surrounding territories. Gardner states that the seed contains 33–35 per cent. of oil, but a report in the *Bulletin* of the Imperial Institute states that 43·1 per cent. was found in seed cultivated in Cyprus, and Fox (*J. I. Eng. Chem.*, 1912, 4, 229) has reported a figure as high as 45 per cent. These latter figures are probably from seeds containing more oil than the usual seed cultivated in China.

Properties.—This oil, which is quite largely used as an edible oil in the

East, has an even higher iodine value and oxygen absorption than linseed oil. On this account it was imported into Europe as a substitute for linseed oil, but has not been particularly successful on account of the peculiar property which the oil has of forming droplets when spread out into a layer. This defect may, however, be overcome by the addition of other oils or by heating to a moderately high temperature the oil then becoming " boiled."

The following constants for the oil due to Tsujimoto are quoted by Lewkowitsch (Vol. II, page 45):

TABLE LXIV.—CONSTANTS OF PERILLA OIL (TSUJIMOTO)

	Seeds from	Colour of Seed.	S.G. 15·5°.	Acid Value.	Sap. Value.	Iodine Value.	n^{15}.
Cold-drawn oils prepared in the Laboratory.	Hokkaido, harvested in 1903 .	Black	0·9342	1·31	193·48	196·45	1·4836
	„ „ .	White	0·9343	0·81	193·35	195·72	1·4837
	„ 1904 .	Black	0·9345	0·98	193·47	197·14	1·4836
	„ „ .	White	0·9342	2·79	193·88	196·75	1·4835
	Aomori 1904	Black	0·9346	1·90	192·17	201·82	1·4840
	Tochigi „	„	0·9343	2·83	193·39	202·45	1·4851
	„ „	„	0·9343	1·99	193·20	200·42	1·4841
	„ „	„	0·9343	0·84	193·31	200·56	1·4841
Commercial oils.	Tochigi, 1904	Black	0·9332	7·62	193·11	193·78	1·4831
	„ „	„	0·9318	6·57	193·48	185·65	1·4822
	„ „	„	0·9344	5·17	193·36	200·46	1·4840
	„ „	„	0·9372	2·69	193·12	190·22	1·4840
			0·9338	2·82	191·67	196·09	1·4835
			0·9325	2·53	189·67	187·48	1·4826

Later workers have published the following:

TABLE LXV.—CONSTANTS OF PERILLA OIL (OTHER OBSERVERS)

Observer.	Source.	S.G. $\frac{15·5°}{15·5°}$	Acid Value.	Sap. Value.	I.V.	n_D^{40}.	Unsap. %
[1] Gardner	Yokohama	0·937	4·3	193·4	193·3	1·4759	..
[2] Gardner and Holdt .	" Orient "	0·935	7·0	193·1	198·8	1·4748	1·07
[3] Imperial Institute .	Cyprus	0·930	..	190·5	185	1·4720	..
[4] Bauer	..	0·930	..	187·4	204·3	1·4785	..

[1] *J.S.C.I.*, 1917, 36, 392. [2] *Ibid.*, 1920, 39, 789A. [3] *Analyst*, 1921, 46, 289. [4] *J.S.C.I.*, 1922, 41, 719A.

Composition.—The composition of the oil has been the subject of several papers by Bauer, but it has not yet been worked out fully. (*J.S.C.I.*, 1922, 41, 719A; 1923, 42, 149A; 1924, 43, B264). Up to the present Bauer

has isolated palmitic acid, which seems to be the only saturated acid present, linolic acid and possibly several geometrically isomeric linolenic acids.

Tests for Purity.—Any serious adulteration will lower the iodine value so that this should be the first determination to make. Where the iodine value is above 190, the colour and appearance good and unsaponifiable matter practically absent, the oil may be classified as genuine.

Polymerised perilla oil.—According to Bauer and Hugel (*J.S.C.I.*, 1925, 44, B250) polymerised perilla oil is a viscous, sticky material which liquifies very slowly on the water-bath, is readily soluble in ether, chloroform, and xylene, but is precipitated by the addition of alcohol to the solutions and has an iodine value of 80·6, as compared with 203 for the unpolymerised oil. Prolonged boiling with concentrated alcoholic potassium hydroxide and subsequent acidification, yielded a viscous mixture of fatty acids having acid value 113·5, and iodine value 89·1. No linolenic acid was detected in the mixture, and linusic acid, *iso*linusic acid, and tetrahydroxystearic acid were not present in the product obtained by oxidising the fatty acids with potassium permanganate solution. Catalytic hydrogenation of the acids resulted mainly in the formation of stearic acid.

Poli Oil

An oil from the seed of *Carthamus oxyacantha* has been described by Barnes and Singh (*Analyst*, 1916, 41, 72), who give different figures from those published for an oil from the same source by Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 991). The plant is stated to grow wild in the North-West of India and to be used for edible purposes by the natives, particularly in famine years. A yellow oil is obtained by expression which has been used as an adulterant of Ghee, so that there seems no reason to suppose that it may not be used legitimately as a substitute for ghee and as a constituent of edible fats. In the following table the figures obtained by Barnes and Singh are compared with those of Crossley and Le Sueur. Barnes and Singh consider that the differences in the figures are due to the fact that the sample examined by Crossley and Le Sueur was not fresh, but they are not easily explained even in this way.

Table LXVI.—Examination of Poli Oil

	Barnes and Singh.	Crossley and Le Sueur.
Specific gravity (15·5°) . .	0·927	0·927
Iodine value	167·4	135·5
Saponification value . .	174·2	189·4
Acetyl value	60·5	..
Acid value	5·9	3·66
Reichert-Meissl value . .	0·6	..
Refractive index (40°) . .	1·4755	..

Poppy-Seed Oil

Source.—Poppy-seed oil is obtained from the seeds of the poppy *Papaver somniferum*, both the white and the black varieties being used for the purpose. The poppy plant is cultivated in Egypt, Asia Minor, Persia, India and other

countries. The opium is obtained from the capsules containing the seed, whilst the oil is, of course, obtained from the seed itself. The seeds contain some 50 per cent. of oil the bulk of which is obtained by cold expression—the seed is usually pressed a second time in the hot when a small quantity of inferior oil is obtained.

TABLE LXVII.—CONSTANTS OF POPPY-SEED OIL (VARIOUS OBSERVERS)

S.G. 15°	Sap. Val.	Iodine Value.	R.M.	n_D^{40}.	Unsap. %.	Sol. Pt. °C.	Acid Val.	Titre. °C.
0·924–0·926	190–195	132–140	0·0 ..	1·4670–1·4690	0·5 ..	−15 to −20	0·3–30·0	16–19 ..

Cf. Thomson and Dunlop, *Analyst*, 1906, 31, 282.

Composition.—Tolman and Munson found that of the total fatty acids of poppy-seed oil about 7 per cent. were solid and 93 per cent. liquid. The solid fatty acids consist for the most part of stearic and palmitic acids, whilst Hazura and Grussner found that the liquid fatty acids consisted of oleic 20, linolic 65, linolenic and isolinolenic acids 15.

The oil contains only a small amount of unsaponifiable matter (about 0·5 per cent.) which, according to Bömer and Winter, consists for the most part of a phytosterol having M.Pt. 136°–137° after eight crystallisations, whilst the acetate has M.Pt. 126°.

Properties and Special Tests.—Cold drawn poppy-seed oil is almost colourless to pale yellow with hardly any odour and a pleasant flavour. No stearine is deposited by the oil. Poppy-seed oil is a good drying oil and by reason of its pale colour is used in the preparation of artists' colours. There are no specific tests for poppy-seed oil with the possible exception of Belliers' test for the detection of this oil in walnut oil, which is described on page 187. (*Analyst*, 1905, 30, 132.)

Adulteration of the oil has not been infrequent in the past sesamé oil (which may, of course, be detected by the Baudouin test) having been used to quite a large extent. As poppy-seed oil gives no precipitate in the insoluble bromide test the addition of many seed oils will be detected in this way; walnut oil for example yields up to 2 per cent.

Lewkowitsch states that as commercial poppy-seed oil is frequently pressed in the same presses as sesamé oil the former frequently gives the reactions of the latter, but Royer (*Analyst*, 1910, 35, 490) states that poppy-seed oils of undoubted purity give no reactions for sesamé in the first pressings, but that they do in the second, and considers that a sample ought not to be condemned as containing sesamé oil, even though it gives reactions pointing to its presence, unless the other chemical and physical constants of the oil confirm the adulteration.

Vuaflart (*J.S.C.I.*, 1911, 30, 965) states that the presence of niger-seed oil in poppy-seed oil raises the solidifying point, but this method would only detect gross adulteration, or complete substitution, at the best.

Utz examined some oils which had been extracted with petroleum ether. He obtained iodine values, shown in the table below, considerably higher than the usual figures which are obtained on expressed oils. It would appear that extraction removes some highly unsaturated bodies.

Source.	I.V.	n_D^{40}.
Indian poppy-seed oil	153·5	1·4681
Levantine poppy-seed oil	157·5	1·4683
German poppy-seed oil	156·9	1·4683

Annett and Sen (*J.S.C.I.*, 1919, 38, 959A) have shown that the cake makes a suitable cattle food.

The oil of the Mexican poppy, *Argemone mexicana*, has been examined at the Imperial Institute (*Analyst*, 1923, 48, 75). The seeds were found to contain 36·5 per cent. of oil, having the following characteristics:

Specific gravity 15°	0·9220
Index of refraction 40°	1·4660
Titre °C.	22·8
Acid value	21·6
Saponification value	192·7
Iodine value	123·7
Unsaponifiable matter	1·14 per cent.
Reichert value	0·0

The oil was found to be unsuitable for paints or for edible purposes and the meal could not be used for cattle feeding owing to the purgative action of the residual oil and the presence of an alkaloid.

This oil has also been examined by K. Bhaduri (*J.S.C.I.*, 1914, 33, 266), who found that the seeds yielded 22·3 per cent. to light petroleum. The expressed oil gradually thickened on keeping and deposited a very small amount of a red crystalline substance, M.Pt. 172° C. The oil solidified at 16°–17° C. The following characteristics were observed: Sp. gr. 0·9117 at 28° C., and 0·9007 at 100° C.; refractive index, 1·46552 at 32° C.; saponification value, 185·5; acetyl value, 27·9; acid value, 146; bromine value, 102·2; Reichert-Meissl value, 0·61; Hehner value, 94·02; glycerol, 15·48 per cent.; Maumené test, 65° C. The fatty acids contained 77 per cent. of liquid acids having the iodine value 147·4. Evidence was obtained of the presence of acetic, valeric and lauric acids.

Safflower Oil

Safflower oil is obtained from the seeds of the saffron plant, *Carthamus tinctorius*, which was formerly cultivated exclusively as a source of the yellow dye, but which is now cultivated for the seeds as a source of oil. The kernels consist of about 40 per cent. of the seed. The whole seed contains 25–37 per cent. of oil, depending to a certain extent upon the source. (Cf. *J.S.C.I.*, 1914, 33, 147; 1916, 35, 696).

The fatty acids consist of about 10 per cent. of solid acids and 90 per cent. of liquid acids. The solid acids consist principally of palmitic and stearic acids, whilst the liquid acids consist almost, if not quite entirely, of oleic and linolic acid (Le Sueur, *J.S.C.I.*, 1900, 19, 104), although

Walker and Warburton (*Analyst*, 1902, 27, 237) found that the fatty acids yielded 0·65–1·65 per cent. of ether insoluble bromides.

The oil is usually of a pale yellow colour possessing slight odour and taste. It has good drying properties which are, however, markedly inferior to those of linseed oil. It polymerises on heating for some hours at a high temperature, the polymerised product being used by the natives as a leather dressing. In the driest districts of the Deccan it is one of the most valued of edible oils.

The constants of the oil have been determined by various observers, notably Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 991), whose figures are given in the table below. The results obtained by other workers practically all lie between the limits here given, but Mann and Kanitkar (*J.S.C.I.*, 1919, 38, 36T) found iodine values of from 111 to 122. (Cf. Howard and Remington, *J.S.C.I.*, 1922, 41, 109A; *ibid.*, 1916, 35, 696.)

TABLE LXVIII.—CONSTANTS OF INDIAN SAFFLOWER OILS

Source.	Sp. Gr. 15°/15°.	Sap. Value.	Iodine Value.	R.M.	Refractive 40° C. Butyro-Refracto-meter.	Acid Value.	Optical Activity in 200 mm. Tube.
C. Provinces .	0·927	192·5	140·1	..	65·2	10·41	8
Bengal . .	0·926	193·3	144·4	..	..	3·68	7
Punjab . .	0·928	186·6	138·6	0·00	..	8·28	..
„ . .	0·927	189·6	144·1	..	..	0·76	10
„ . .	0·925	187·4	129·8	..	..	2·90	12
Hyderabad .	0·928	187·9	138·6	..	..	2·58	14
Bombay . .	0·926	187·2	143·4	..	65·2	2·67	8
Cawnpore .	0·927	189·4	141·4	0·0	..	5·92	7
Bombay . .	0·927	191·3	149·9	0·0	..	6·20	4
Cawnpore .	0·925	190·5	141·1	..	..	20·02	..
Madras . .	0·928	192·4	142·9	..	..	4·12	6

STILLINGIA OIL

Stillingia oil is obtained from the seeds of *Stillingia sebifera* which is largely cultivated in China. The seeds contain two kinds of oil, that in the mesocarp yielding Chinese vegetable tallow, whilst the kernels yield a drying oil which, although not exported to any extent, might be used as a substitute for linseed oil. The oil from the mesocarp is described under stillingia tallow on page 299.

In some cases the seed oil is expressed along with the vegetable tallow but in others the seeds are crushed after the vegetable tallow has been removed. The seeds contain about 20–23 per cent. of a light yellow oil resembling linseed oil, although its drying powers, whilst still good, are inferior to the latter. When treated in the insoluble bromide test considerable quantities of bromides are obtained which melt (according to Sprink-

meyer and Diedrichs) at 147°. The oil is strongly lævorotatory, having an optical rotation in a 200 mm. tube of −6° to −7°. The following values have been obtained for this oil by different observers (*J.S.C.I.*, 1901, 20, 261; 1914, 33, 1098):

TABLE LXIX.—CONSTANTS OF STILLINGIA OIL

Observer.	S.G. 15°.	Acid Val.	Sap. Val.	R.M.	Iodine Value.	Unsap %.	n^{40}.	Titre.
Tortelli and Ruggeri.	0·943	12·2	210·4	0·9	160·6	1·45	1·4736	12·2
Nash	0·940	..	..	..	160·7	..	1·4765	..
Diedrichs. . . .	..	1·2	209	1·0	155	..	1·4763	..

SUNFLOWER-SEED OIL

Sunflower-seed oil is obtained from the achenes of the common sunflower, *Helianthus annuus*. The seeds are cultivated on a large commercial scale only in Central and South-Eastern Europe (*J.S.C.I.*, 1892, 11, 470; 1916, 35, 696), although India, China and the United States also produce considerable quantities. The seeds are largely used as a poultry food and the remainder of the plants might be a useful source of potash. The best Hungarian seeds contain 28 to 30 per cent. of oil, which is practically all contained in the kernels which constitute nearly 50 per cent. of the seeds. Russian and Sudan seeds contain considerably less oil. The cold-pressed oil is an excellent edible oil, being largely used as a salad oil and for the manufacture of margarine.

The composition of the oil has been studied by Jamieson and Baughman, who examined at length a sample of oil obtained from American seed. They found that the oil had the following composition:

	Acid.	Per Cent.
Glycerides of	Oleic	33·4
	Linolic	57·5
	Palmitic	3·5
	Stearic	2·9
	Arachidic	0·6
	Lignoceric	0·4
	Unsaponifiable matter	1·2

The oil is pale yellow in colour and has little odour or taste. It dries slowly when exposed to the air, but is very distinctly inferior to linseed in this direction. The following characteristics have been observed by various workers:

TABLE LXX.—CHARACTERISTICS OF SUNFLOWER-SEED OIL

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	n_D^{40}.	Sol. Pt. °C.	Titre. °C.	Unsap. %.	Acid Val.
De Negri and Fabris .	0·926	188–189	119·7 120·2	..	..	18	..	..
[1] Holde	0·924	193	135	..	Partially solid −17	..	..	11·1
[2] Thomson and Dunlop	0·922[7]	189·3	131·3	1·4669	..	..	0·70	2·4
[3] Imperial Institute .	0·924 0·926	188–194	120–135	..	..	..	..	..
Thorner	..	193–194	129	1·4684	..	17	..	..
[4] Jamieson and Baughman	..	188·0	130·8	1·4663	..	..	1·20	2·3
Other observers . .	0·919[5]–0·926	191·7-193·3	106[6]–136	1·4683	−16 to −18·5	18–20	0·31–0·72	6·2

[1] *J.S.C.I.*, 1894, 13, 892. Oil extracted with petroleum spirit. [2] *Analyst*, 1906, 31, 282. [3] *J.S.C.I.*, 1916, 35, 696. [4] *Analyst*, 1923, 48, 126. [5] Apparently rather low. [6] Bolton and Revis from white seeds. [7] Russian.

The oil gives no reaction with either Halphen's or Baudouin's reagent. It is sometimes used as an adulterant of olive oil and as a substitute for cotton-seed oil and other seed oils. For the composition of sunflower-seed silage, see *J.S.C.I.*, 1920, 39, 170A, and for the lipase of sunflower seeds see *Ibid.*, 1924, 43, B23. For polymerised sunflower oil see *Ibid.*, 1925, 44, B250.

WALNUT OIL

Walnut oil is obtained from the nuts of the common walnut *Juglans regia*, the kernels of which contain about 65 per cent. of oil. The fully ripened kernels are expressed firstly in the cold, giving an almost colourless clear oil having an agreeable odour and taste which is used as an edible oil in some parts of Europe, and secondly in the hot, giving a green oil of unpleasant taste which is used for technical purposes.

The solid fatty acids of walnut oil consist of myristic and lauric acids, whilst the liquid acids which largely predominate consist mostly of linolic acid (80 per cent.) with smaller quantities of oleic, linolenic and isolinolenic acids. The oil yields less than 2 per cent. of precipitate in the insoluble bromide test which serves to detect any material addition of linseed oil, a possible and likely adulterant. Other likely adulterants are cotton seed,

sesamé and arachis oils, which may be detected by the application of the appropriate tests. Poppy-seed oil has also been used as an adulterant, and a method has been devised by Bellier for its detection. This method, which is given below, is not specific although the indications should not be given by a pure oil which is not very rancid.

In Bellier's test, 1 c.c. of the oil is warmed with 5 c.c. of a solution of alcoholic potash, containing 16 grms. of potassium hydroxide in 100 c.c. of 92 per cent. alcohol, until a clear solution is obtained. The test-tube is corked and warmed in a water-bath for half an hour to 70°. Then so much of a 25 per cent. solution of acetic acid is run in, as is required to neutralise exactly the 5 c.c. of alcoholic potash solution (this must be ascertained in a blank test). The test-tube is then corked, placed in water at 25° and finally in water at 17°–19°, being shaken frequently. Pure walnut oil gives only a minute precipitate, which hardly covers the bottom of the test-tube, whereas poppy-seed oil yields a copious precipitate.

The following may be taken as average values for the usual determinations: Sp. gr. 15°/15°, 0·926; saponification value, 192–197; iodine value, 142–150; refractive index at 40°, 1·4690–1·4705; solidification point, below −14°; titre, 14°–16°. (Cf. Pecan oil, page 209.)

CHAPTER XI

Soya-Bean Oil

Source.—Soya-bean oil is obtained from the seeds of *Glycine Soja*, S et Z., *Glycine hispida*, Maxim (other synonyms are known), a plant which is indigenous to China, Japan and neighbouring countries. The soya bean and its products have been known and used for thousands of years in the past, but it was not until 1908 that the first consignment of the beans was received in Europe, although for a number of years previous to this the meal had been imported in large quantities. (U.S. Dept. of Agri., *Analyst*, 1910, 35, 20.) The seeds contain some 16–19 per cent. of oil, whilst about 10–12 per cent. are yielded by expression on the commercial scale. (Fellers has found 14·6–25·6 per cent. of oil in 28 varieties of seed.) The following remarks by Toch (*J.S.C.I.*, 1912, 31, 572) give an excellent idea of the European knowledge of the plant at the time they were written:

"In 1909 soya-bean oil as a paint oil was practically unknown. Since that time many investigators have published more or less conflicting articles concerning soya-bean oil, and even the physical and chemical constants of soya-bean oil vary to some extent. Owing to the fact that discordant results were continually obtained, it is only within the last year that it has been possible to state with some degree of certainty whether soya-bean oil is a substitute for linseed oil, an adjunct to it, or neither. The reason for this uncertainty and discrepancy is apparent when it is stated that the author himself has experimented with 33 different varieties of soya beans, and in the records of the Department of Agriculture at Washington no less than 280 varieties of soya beans are listed.

"From time immemorial, the soya bean has been grown in China and Japan, where it has served as one of the staple articles of food, and as the basis for a number of food preparations. In Europe and the United States, however, the value and uses of the bean have been but little appreciated until very recently (1908), when, on account of the scarcity in the cotton seed supply of the world, soap and glycerin manufacturers began to turn their attention to its possibilities. In Manchuria, where by far the major portion of the soya beans are grown, practically the entire crop is available for export. The following figures taken from the Consular Reports will serve to show the extent of the soya bean industry during the past three years:

	1909. Tons.	1910. Tons.	1911. Tons.
Total shipments of beans from Far East . . .	1,470,870	1,200,000	1,500,000
Imported into Europe .	400,000	500,000	340,000

"As the above statistics indicate, China and Japan retain for domestic consumption practically two-thirds of the available supply of beans. The sugar plantations in Southern China and the rice-fields of Japan annually consume enormous quantities of soya beans and bean cake as fertiliser, while the extracted oil is used as food by the natives.

"In connection with the use of soya beans and soya-bean oil for edible

purposes, it may be mentioned that there has been recently established at Les Vallees, France, a thoroughly up-to-date factory for the production of a wide assortment of food products from soya beans. Among the more important of these may be mentioned : milk, cheese, casein, oil, jellies, flour bread, biscuits, cakes and sauces. According to Dr G. Brooke, Port Health Officer of Singapore, the soya bean, more nearly than any other known animal or vegetable food, contains all the essential and properly proportioned ingredients of a perfect diet.

" All soya beans are leguminous plants, which do not tend to deplete the soil of nitrogen, for the typical soya bean plant is self-nitrifying and grows in almost any soil that contains a reasonable amount of potash. In addition to this, the soya bean enriches even very poor ground when used as a ground manure. This is done by planting the seed promiscuously, allowing it to grow to a height of about 6 inches, and then turning it in. In this way both nitrogen and potash are given to the soil for future use in an available form. The average height of the soya bean plant is about 36 inches. The pods resemble those of our sweet-pea. They are about 2½ inches in length and are covered with a hairy growth. Generally there are two or three beans in each pod. After the oil is extracted from the bean the cake appears to be very valuable as a cattle food, while the leaves and stalks, if collected and set in a dry place, make excellent silage. We thus have practically the entire plant available for use, with the exception of the roots.

" The average composition of the soya bean varies within fairly narrow limits among the different varieties of soya beans."

In the following table are listed the analyses of a few of the varieties of soya beans :

TABLE LXXI.—ANALYSIS OF SOYA BEANS

Variety.	Water.	Proteins.	Fat.	Nitrogen Free Extract.	Fibre.	Ash.
	%	%	%	%	%	%
Austin	8·67	36·59	20·55	24·41	4·00	5·78
Ito San	7·42	34·66	19·19	27·61	5·15	5·97
Kingston	7·45	36·24	18·96	26·28	4·79	6·28
Mammoth	7·49	32·99	21·03	29·36	4·12	5·01
Guelph	7·43	33·96	22·72	25·47	4·57	5·85
Med. Yellow . . .	8·00	35·54	19·78	26·30	4·53	5·85
Samarow	7·43	37·82	20·23	23·65	5·05	5·82

The later commercial conditions and the various methods used and products obtained are well described in the following abstract of a paper by Satow (*J.S.C.I.*, 1922, 41, 64A) :

" There are upwards of thirty varieties of bean which may be classified into yellow, blue and black. The first contain most protein and oil, the last the least. The protein content varies from 35 to 40·5 per cent. and the oil content from 15·4 to 20·9 per cent. The mean analysis of sixteen different varieties was : Water, 10·2 per cent.; proteins, 37·8 per cent.; oil, 18·9 per cent.; carbohydrates, 23·5 per cent.; fibre, 5·2 per cent.; ash, 4·4 per cent. The bean of the Hokkaido contains the most protein and the least fibre. The Korean bean contains much carbohydrate and less protein. The beans contain an average of about 5 per cent. of soluble protein and

0·01–0·04 per cent. of non-protein nitrogenous matter. The following specification is given for a good industrial raw material : Crude protein over 40 per cent. of the dry bean, soluble protein under 4 per cent., available protein 38 per cent.; the beans should be yellow or brownish-yellow and should contain not more than 13 per cent. of water; sp. gr. 1·308–1·310. The carbohydrates consist mainly of non-reducing sugars with little or no starch. The cell membrane consists of galactan or hemicellulose, with a little free cellulose. The presence of the hulls in the crushed bean reduces the speed of extraction of the oil and the yield and gives the oil and protein a brown colour. The hulls may be easily removed by passing the beans through a disintegrator at about 65°. *Oil Extraction.*—The yield of oil is improved by air-drying the beans to a moisture content of about 7·5–12·5 per cent. before crushing. Care must be taken not to oxidise the oil. Benzine is the most suitable commercial solvent. For efficient extraction the conditions are : Complete disintegration of the cellular structure, high temperature and agitation during extraction. Steam-jacketed rotary drum extractors are satisfactory, but the drum must not be rotated so rapidly as to pulverise the beans. The extraction should be repeated with fresh solvent not more than three times. Injury to the proteins is avoided by keeping the temperature below 45° and the water content below 13 per cent. The solvent must not be recovered by direct steaming of the meal, but by the use of a vacuum. An extractor, 5 ft. in diameter and 15 ft. long, with a capacity of 5000 lb. of rolled beans, is described, having a specially designed stuffing-box to prevent leakage of solvent, air, or steam. A suitable speed of rotation during extraction is 2 r. p.m., each charge of solvent being kept in for 1 hour. The solvent can be completely removed from the meal by finally raising the vacuum to 29 inches. For the recovery of the solvent condensers are used on the vacuum side of the pump, but the exhaust is delivered into a trap to catch the condensing solvent and finally passed up a tower of coke moistened with vegetable oil or kerosene. The loss of solvent is less than 1 per cent. The solvent is removed from the oil in the usual way by steam distillation, and the oil bleached by emulsification with a 1 per cent. solution of sodium peroxide. The emulsion is broken with dilute sulphuric acid and the oil allowed to settle or recovered by means of a centrifugal machine. *Protein Extraction.*—The soluble carbohydrates are removed from the meal by washing with very dilute acetic acid. The protein is then extracted in three stages, viz., with water, with 0·2–0·4 per cent. sodium sulphite solution, and with 0·2 per cent. sodium hydroxide solution. 20–30 per cent. of the total available protein is extracted in the first stage, a further 50 per cent. in the second, and the total yield is about 95 per cent. In each case from five to eight extractions are necessary. The protein extracted in the second stage is suitable for the manufacture of celluloid-like articles, but that from the third stage is suitable only for lacquers or coating materials. The best quality products are obtained by purifying by precipitation with sulphurous acid, sulphuric and acetic acids being the next best precipitants. Heat rapidly hydrolyses the protein into non-precipitable forms and must be rigorously excluded in the preparation of plastic materials of good quality. The excess water is separated from the precipitated proteins by means of a continuous vacuum filter, and then by means of hydraulic pressure, the water content being reduced to 55 per cent. The protein is finally dried at the lowest temperature and highest vacuum and in as short time as possible. The dry protein is very tenacious and can only be ground in high-speed disintegrators; it is then suitable for the manufacture of plastic materials, lacquer, enamel, or imitation leather.

The soluble carbohydrates, which amount to 10–12 per cent. of the meal treated, can be worked up into syrup or converted into alcohol or lactic acid by fermentation. The bean residue consists of fibre, galactin, and protein and can be used for cattle food or as an ingredient of linoleum-like products."

Composition.—The composition of soya-bean oil has been studied by several observers. Keimatsu (*Analyst*, 1911, 36, 513) found 12 per cent. of saturated fatty acids which were chiefly stearic and palmitic acids and some 80 per cent. of unsaturated acids about half of which yielded a hydroxy acid melting at 158°–159°. Ordinary linolic acid and oleic acid together formed about 15 per cent. of the unsaturated acids.

Matthes and Dahle (*J.S.C.I.*, 1911, 30, 1124) found the oil to contain 94–95 per cent. of fatty acids, of which about 15 per cent. consist of saturated acids (palmitic acid) and about 80 per cent. of liquid unsaturated acids. The latter were found to consist of about 70 per cent. of oleic acid, about 24 per cent. of linolic acid, and about 6 per cent. of linolenic acid. They found the unsaponifiable matter to be about 0·7 per cent., of which about 55 per cent. was a crystalline solid of which 97 per cent. was a phytosterol which had M.Pt. 139°.

Smith (*Analyst*, 1922, 47, 400) found that the composition of the mixed fatty acids obtained from soya-bean oil having an iodine value of 134 was—linolenic acid 2 to 3 per cent., linolic acid 55 to 57 per cent., oleic acid 26 to 27 per cent., saturated fatty acids 9 to 10 per cent.

Baughman and Jamieson (*J.S.C.I.*, 1923, 42, 149A) have examined the mixed fatty acids by methods depending upon the separation of tetrabromides, the lead-salt-ether method and the method of alcoholysis. As a result of a considerable amount of work they arrive at the following composition for the oil:

Acid.	Per Cent.
Linolenic	2·3
Linolic	51·5
Oleic	33·4
Palmitic	6·8
Stearic	4·4
Arachidic	0·7
Lignoceric	0·1
Unsaponifiable matter	0·6

This result of Baughman and Jamieson agrees fairly well with the previous investigators and may be taken as representing an average sample of soya-bean oil. Myddleton and Barry (*Fats : Natural and Synthetic*, page 109), have obtained by a somewhat similar method the following results for the composition of the mixed fatty acids: Palmitic, 11; stearic, 2; oleic, 20; linolic, 64; linolenic, 3. Brightman (*J.S.C.I.*, 1919, 38, 120T) found that a deposit in a refined soya-bean oil consisted of a complex sulphonated glyceride. The results of Baughman and Jamieson have been substantially confirmed by Wallis and Burrows (*J.S.C.I.*, 1924, 43, 838B) using the method of Twitchell. These authors have found in the fatty acids:

Unsaturated acids	88
Palmitic acid	10
Stearic acid	2
Arachidic acid	1

TABLE LXXII.—CHARACTERISTICS OF SOYA-BEAN OIL (VARIOUS OBSERVERS)

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	Sol. Pt. °C.	Acid Value.	R.M.	Pol.	n_D^{40}.	Titre. °C.	Unsap. per cent.	Fatty Acids M.Pt °C.
[1] Imperial Institute	0·924–0·927	190·6–192·9	121·3–124·0	..	..	..	..	..	..	..	..
[2] Oettinger & Buchta	0·925–0·927	192·4–194·0	132·9–135·0	−8 to −16	0·0–5·2	0·5–0·6	..	1·4677–1·4683	..	0·39–0·59	..
[3] Keimatsu	0·927	190	132–135	−15 to −16	..	..	..	..	16	..	..
[4] Matthes & Dahle	0·926–0·927	192·3–194·3	131·3–132·6	−12	5·7–1·7	0·8	0·8–1·1	1·4680	..	..	..
[5] Fellers	0·925	190–195	123·2–132·3	..	0·2–2·6	..	..	1·4686	..	..	..
Bolton & Revis	0·924–0·926	190–193	130–136	..	3 or less	..	..	1·4675–1·4682	..	0·3	26–29

[1] *Analyst*, 1910, 35, 20. [2] *Analyst*, 1911, 36, 358. [3] *Analyst*, 1911, 36, 513. [4] *J.S.C.I.*, 1911, 30, 1124. [5] *J.S.C.I.*, 1921, 40, 153A.

The following table compiled by Toch (*J.S.C.I.*, 1912, 31, 572) gives the constants for oils from various sources:

TABLE LXXIII.—CONSTANTS FOR SOYA-BEAN OILS FROM VARIOUS SOURCES (TOCH)

Name.	Colour of Seed.	Colour of Oil.	Sp. gr. 15° C.	Acid Value.	Iodine Value.
Meyer . . .	Brown	..	0·9264	0·44	127·0
Peking . . .	Black	Extremely pale	0·9279	0·14	135·4
Haberlandt . .	Straw-yellow	..	0·9244	0·00	129·8
Farnham . .	Straw-yellow	..	0·9234	0·65	131·8
Taha	Black Olive Saddle	Pale amber somewhat deeper than above	0·9248	0·16	127·0
Mammoth . .	Straw-yellow Brown	Pale amber somewhat deeper than Meyer, etc.	0·9222 0·9248	0·47 0·17	118·2 129·3
Edward . . .	Straw-yellow	Med. amber	0·9257	1·14	124·6
Shanghai . .	Black	Same depth as previous olive tone	0·9241	0·63	127·8
Refined linseed oil	..	..	0·933	1·0	180·1

Properties and Special Tests.—Soya-bean oil is a light-yellow to pale-brown oil having a slight odour and taste; it deposits no stearine at ordinary

temperatures. In its drying properties it stands in the semi-drying class and may be " boiled " and used for addition to linseed oil as a paint material. In the Livache test it gives an absorption of about 8, compared with about 15 for linseed oil. The oil is an excellent edible oil and has been used in quite large quantities in the manufacture of margarine. There is no specific test by which this oil may be detected in admixture with other oils, whilst the usual colour reactions such as Halphen's give negative results. The value of soya-bean oil usually lies below that of other seed oils, so that there is little inducement for adulteration. Cotton seed and sesamé oils would be detected by the Halphen and Baudouin tests whilst linseed, in the unlikely event of its presence, would be indicated by an increased iodine value and an increase in the insoluble bromide value which is about 7 (7·8 Eibner and Muggenthaler). Tschudy (*Analyst*, 1921, 46, 513) considers that this method may give results differing by +13 to −9 per cent. from the actual amount of linseed oil present in mixtures.

The iodine value of the oil usually lies round about 132–135, but in some cases (see table above) lower values than these have been obtained, whilst Ingle (*J.S.C.I.*, 1911, 30, 345) has found oil from greenish soya beans having an iodine value as high as 158, but these are, apparently, exceptional cases. Low (*J.S.C.I.*, 1920, 39, 550A) found, on one sample, an iodine value of 138·5.

A colour reaction with uranium nitrate has been suggested for this oil by Settimj (*Analyst*, 1913, 38, 36) which is carried out by shaking a mixture of 5 c.c. of the oil with 2 c.c. of chloroform and 3 c.c. of a 2 per cent. aqueous solution of uranium nitrate, an intense yellow emulsion is produced, whilst other seed oils give no such colour except olive oil which sometimes gives a slight reaction.

Practically the same test has been suggested by Newhall (*Analyst*, 1921, 46, 94), who further states that linseed oils give a slightly brownish emulsion whilst bleached or deodorised soya-bean oils do not give the reaction.

This test has, however, been examined by Utz (*J.S.C.I.*, 1922, 41, 222A), who states that it fails under many conditions and is not sufficiently characteristic to serve for the distinction of soya-bean oil from other oils or fats.

Dall Acqua (*J.S.C.I.*, 1921, 40, 153A) states that the oil has different electrical properties from those of other seed oils, and finds that an electroscope of the Elster and Geitel pattern is discharged in only a fraction of a second through soya-bean oil whilst other oils required from 15 to 100 seconds.

Brill (*J.S.C.I.*, 1916, 35, 1077) has found that some varieties of soya beans, particularly those grown in Japan, contain a substance which is soluble in alcohol and ether, volatile in steam, crystallisable, and yields a violet colour with ferric chloride. This substance, which is probably Brand's maltol (*J.S.C.I.*, 1894, 13, 896; 1895, 14, 378), does not give a reaction with Jorissens' test for salicylic acid (a red colouration when the solution is heated with potassium nitrite, acetic acid and a trace of copper sulphate).

Hydrogenated Soya-Bean Oil.—Constants for the oil after hydrogenation have been given by Mellana (*J.S.C.I.*, 1914, 33, 701), who states that a sample of hydrogenated soya-bean oil had M.Pt. 68°, M.Pt. of fatty acids 66°, titre 61·2°, saponification value 190·9, and iodine value 15·2, whilst Myddleton and Barry (*loc. cit.*) found in the fatty acids of a hydrogenated soya-bean oil an iodine value of 58 (the original iodine value of the untreated oil was 137·9), palmitic acid 11, stearic acid 26, oleic 34, linolic 4, and " new acids of hydrogenation " 25.

Soy Oil.—Tsujimoto and Ueno (*J.S.C.I.*, 1915, 34, 1259) have described " soy " oil and " saké " oils. They state that " ' Soy ' oil is a mixture of

soya-bean and wheat oils obtained as a by-product in the brewing of soy (yield 0·25 to 0·3 per cent. by volume). It is a dark red to brown liquid or semi-solid mass with an aromatic odour of soy. 'Saké' oil consists chiefly of rice oil and is found floating on the surface after the fermentation of sake (yield 0·01 to 0·02 per cent. by vol.). It is an orange-yellow liquid with an odour of sake. Samples of these oils had the following characters:

TABLE LXXIV.—COMPARISON OF SOY AND SAKÉ OILS

	Soy Oil.		Saké Oil.
	1.	2.	
Sp. gr. 15°/4°	0·9000	0·9835	0·9031
Solidif. pt. ° C.	−5	−13	Turbid at 0
Acid. value	59·24	55·03	22·56
Saponif. value	184·12	182·81	179·11
Iodine value (Wijs)	127·79	133·22	101·56
Refractive index (20°)	1·4650	1·4633	1·4660
Unsap. matter per cent.	2·88	2·72	..

Soy oil, which is best refined by reduction with zinc dust and sulphuric acid, followed by treatment with Kambara earth, is a commercial product used in the manufacture of low-grade soaps. Saké oil is not yet a commercial article."

Soya-Bean Miso Oil.—Kodama (*J.S.C.I.*, 1924, 43, 564B) has investigated the nature of the oil of this Japanese food. He states that " miso is a staple Japanese food made from polished rice fermented with *Aspergillus oryzæ*, mixed with steamed soya beans, salt and water. The oil was extracted from the dried miso of two different varieties. It had the same odour and taste as soya-bean oil and the following characters: d. 0·9466–0·9471; acid value, 22·5–77·7; saponif. value, 211–235; iodine value, 117–132; Hehner value, 93·5–98·0; Reichert-Meissl value, 3·56–7·46. The decolorisation of the oil with animal charcoal materially altered the above characters; the iodine value was greatly decreased, and the saponification and Henher values were increased, the oil becoming nearly solid. The oil shows a greater Reichert-Meissl value and a smaller iodine value than soya-bean oil."

The detection of soya beans in cows' milk has been studied by Nakayasu (*Analyst*, 1922, 47, 398), who states that " Soya-bean albumin (or bean milk) is made in Japan by soaking the washed beans for 10 hours in water, then grinding them, and boiling and filtering the product. The filtrate of 'soya-bean albumin' has a sp. gr. of about 1·03, and a sample examined by Suda contained 10·57 per cent. of total solids, 2·27 per cent. of fat, 4·88 per cent. of albumin, 2·72 per cent. of carbohydrates, 0·07 per cent. of fibre, and 0·6 per cent. of ash. Unlike rice milk, the bean carbohydrates cannot be detected in milk by the iodine test. A sensitive test, however, has been based upon the fact that glycinine, the main constituent of soya-bean protein, is soluble in alkali solution, and is then readily oxidised on exposure to the air, becoming yellowish-brown in colour, whereas casein and lactalbumin do not become yellow on similar treatment. If, on treating 10 c.c. of milk with 4 or 5 drops of a 28 per cent. solution of potassium hydroxide a yellow colouration is produced, the presence of soya-bean protein is indicated."

A synthetic production described as soy-bean milk has been the subject of various patents. Monahan and Pope (*J.S.C.I.*, 1916, 35, 271) grind the beans to a coarse powder, add a little coconut oil, and emulsify the mass with an equal amount of water at a temperature above 27° in the presence of sodium bicarbonate and lime. The liquid portion is separated and heated for several hours below its boiling-point (cf. *J.S.C.I.*, 1916, 35, 751 and 903).

Remy has published (*J.S.C.I.*, 1922, 41, 681A) an examination of such a substance which he found to be a yellowish-white liquid having a sickly sweet taste and a faintly-acid reaction. It had the following composition : Water, 88·93 per cent.; dry matter, 11·07 per cent.; fat, 3·06 per cent.; non-fatty solids, 8·01 per cent.; protein, 2·96 per cent.; starch, 0·57 per cent.; glucose, 2·48 per cent.; mineral matter, 0·63 per cent.; alkalinity of ash, 6·44 c.c. of N/1 acid; bacteria per c.c., 4000.

The following additional references may be studied for further information on the points mentioned :

" The Denaturation of Soya Beans and Oil in Australia." *J.S.C.I.*, 1912, 31, 593, 782; 1914, 33, 837.

" The Composition of Soya Beans." *Analyst*, 1910, 35, 20; 1923, 48, 125.

" The Uses of Soya Beans." *J.S.C.I.*, 1911, 30, 38, 45.

" The Lipase and other Enzymes of Soya Beans." *J.S.C.I.*, 1915, 34, 366; 1920, 39, 340A.

" Soya-Bean Meal Poisonous by Extraction with Trichlorethylene." *J.S.C.I.*, 1916, 35, 1175.

" Yield, Nitrogen Content and Nutritive Value of Soya Beans." *Analyst*, 1923, 48, 234. *J.S.C.I.*, 1917, 36, 1021, 1286; 1923, 42, 1034A.

" Production of Soya Beans." *J.S.C.I.*, 1919, 38, 84A.

" The Effect of Growing Beans under Abnormal Conditions." *J.S.C.I.*, 1919, 38, 588A.

" Driers for Soya-Bean Oil and Uses for Paints." *J.S.C.I.*, 1919, 38, 833A.

" Artificial Petroleum from Soya-Bean Oil." *J.S.C.I.*, 1922, 41, 242A, 360A.

" Losses in the Refining of Soya-Bean Oil." *J.S.C.I.*, 1923, 42, 561A.

" Environmental Factors Affecting the Protein and Oil Content (and Iodine Value of Oil) of Soya Beans." *J.S.C.I.*, 1925, 44, B214.

" Soya Beans and Soya-Bean Bread." *J.S.C.I.*, 1925, 44, B332.

" The Vitamin Content of Soya Beans." C. Hornemann, *J.S.C.I.*, 1925, 44, B470.

CHAPTER XII

SEMI-DRYING OILS

Oil from Balanites Species

Oils have been obtained from various species of Balanites. These would appear to have value as edible oils, and indeed are valued locally, but the supply is in most cases small and there would not appear to be much chance of their commercial exploitation at the moment.

The fruit of *Balanites Œgyptica* is thus described by Lewkowitsch quoting Suzzi : " The fruit, which is at first green, becomes red on ripening, and in its dry state somewhat resembles a date. It consists of a thin, brittle shell, enclosing a fleshy mass of gummy consistence which firmly adheres to the hard stone; the latter furnishes the kernels. The kernels contain 49·64 per cent. (Suzzi) to 41·2 per cent. (Milliau) of fatty matter."

The Imperial Institute found that the oil consisted of the glycerides of oleic acid 33 per cent., linolic acid 33 per cent., palmitic and stearic acids 34 per cent.

Arnold (*Analyst*, 1912, 37, 256) has described the East Africa nuts, where they are known as Mkonga nuts. He found the Reichert value 0·6, the Polenske value 0·4, and the iodine value of the insoluble acids 82·9.

The fruits of *B. Maughamia* have been described by Sprague and by Bolton and Jesson (*Analyst*, 1915, 40, 3) in the following words : " The tree is a native of Portuguese East Africa, where it is said to be abundant in the Lebombo mountains, and known as ' Manduro.' Specimens of the tree and fruit have only recently been received in this country, and have been fully dealt with botanically by T. A. Sprague in the *Kew Bulletin*, *Misc. Inform.*, *No.* 4, 1913, who described the fruit as ' a drupe, oblong-ellipsoid, 1½ to 1¾ inches long, 1 inch in diameter or rather more, with a deep basal depression and a smaller apical one, at the bottom of which are ten scara left by the pedicel and stype respectively, longitudinally five grooved in the upper part; epicarp, crustaceous; mesocarp, fibrous and spongy; endocarp, woody, 1½ to 2 inches thick. Seed-coat, buff-coloured.' The above parts are present in the following proportions :

Epicarp mesocarp (pulp)	56 per cent.
Endocarp	33 ,,
Kernel	11 ,,

" The Imperial Institute, in their *Report No.* 88, publish some figures for the oil from the kernels. Oil is, however, contained in both the outer sticky pulp and in the kernels; the latter have a high content of a clear pale yellow valuable oil, which is, unfortunately, not likely to be obtained at present on a commercial scale owing to the difficulty of removing the spongy, sugary pericarp. The sticky pulp and the olive-green oil which it contains, have an overpowering smell of butyric acid, while the kernel oil has only a slight butyric odour."

The oil from the fruits of *B. tieghemi* has been described by Hébert (*J.S.C.I.*, 1911, 30, 497), who states that the yield of fat from the kernels is 10 per cent., whilst that from the entire seed is only 2 per cent. This

author found 63 per cent. of solid acids and 37 per cent. of liquid acids, but his results stand in need of confirmation; particularly the high Reichert value of 6·0.

The analytical characteristics of the various oils as obtained by the above observers are contained in the following table:

TABLE LXXV.—ANALYTICAL CHARACTERISTICS OF OIL OF BALANITES SPECIES

Source.	Observer.	S.G. 15°.	Sap. Value.	I.V.	Sol. Pt. °C.	Titre. °C.	M.Pt. Acids. °C.	Acid Val.	Unsap. %	n_D^{40}.
B. ægyptica	Suzzi	0·920	194·1	105·0	3 to 0	31	36	0·9	..	..
B. ægyptica	Gordon College	..	186·5	99·2	..	..	..	..	..	..
B. ægyptica	Imperial Institute	[1] 0·919 [2] 0·919	196·7 194·2	92·5 98·2	.. ..	34·6 34·0	.. ..	5·0 1·4	0·6 ..	.. ..
B. ægyptica	[3] Arnold	0·917	195·6	77·2	8 turbid	..	..	8·5	0·07	..
B. maughamii	[4] Bolton & Jesson	.. ..	.. [5] 191·5	[4] 77·5 100·6	.. −1	.. ..	.. ..	157 2·4	.. 9·9	1·4605 1·4639
B. tieghemi	[6] Hébert	0·908	..	121·0	..	..	35	9·4	..	..

[1] *Analyst*, 1909, 34, 167. Nigeria. [2] Sudan. [3] *Analyst*, 1912, 37, 256. [4] *Analyst*, 1915, 40, 3. Pulp oil. [5] Kernel oil. [6] *J.S.C.I.*, 1911, 30, 497.

BEECH-NUT OIL

Beech-nut oil is obtained from the kernels of the fruit of the beech-tree, *Fagus sylvatica* L. The nuts contain 23 per cent. and the kernels 43 per cent. of oil. The cold-drawn oil is used as an edible oil. Beech-nuts may contain a poisonous principle, fogin (Vaubel, *J.S.C.I.*, 1919, 38, 729A), which is a trimethylamine derivative. This is reputed to have caused the poisoning of horses fed upon the seed cake and it is recommended that, to obtain a wholesome oil, the sound kernels be expressed not later than February. Beech-nut cake was suggested by Honcamp (*J.S.C.I.*, 1919, 38, 841A) as a war-time feed for ruminants as the kernel cake corresponds in nutritive value to cotton-seed cake. The toxic effect of beech-nut meal was later ascribed by Sabalitschka (*J.S.C.I.*, 1920, 39, 556A) to the presence of about 0·5 per cent. of oxalic acid which probably occurs as potassium hydrogen oxalate. This may be removed by extracting the meal with about five volumes of water for several hours. The cold-drawn oil is pale yellow in colour with a slight agreeable smell; it becomes turbid on cooling. It has somewhat inferior drying properties to cotton-seed oil.

The following characteristics have been observed:

TABLE LXXVI.—CHARACTERISTICS OF BEECH-NUT OIL

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	Sol.Pt. °C.	M.Pt. Acids. °C.	Titre. °C.	Acid Value.	n_D^{40}.
De Negri and Fabris . .	0·922	191·1	111·2	−17	..	17	..	..
Higuchi[1] . .	..	201·5	112·2	..	17	..	0·78	..
Vaubel . . .	0·910 0·917	..	..	..	..	..	..	1·4628– 1·4641

[1] *J.S.C.I.*, 1916, 35, 261.

BRAZIL-NUT OIL

This oil is obtained from the well-known "Brazil nuts," which are yielded by the tree *Bertholletia excelsa* largely cultivated in South America. The oil is said to be used for edible purposes in the countries of origin. The oil has a pale yellow colour with pleasant taste and little odour. It readily deposits stearine and soon becomes rancid. The oil yields no insoluble bromide. The kernels contain some 65 per cent. of oil. The oil has been examined by De Negri and Fabris, Lewkowitsch and Grimme (*Analyst*, 1911, 36, 21).

Specific gravity at 15° . . .	0·918
Solidifying-point °C.	−3
Saponification value	193–202
Iodine value	91–106 *
Titre test °C.	32
M.Pt. of acids °C.	28–30
Iodine value of acids	99–108

The paradise nut (*Lecythis zabucajo*), the tree of which grows extensively in Brazil, is very similar to the Brazil nut. De Negri has found: sap. value 173·6, acid value 3·2, iodine value 71·6, n^{40} 1·4578, titre 28·5°.

OILS OF SEEDS OF THE CITRULLUS SPECIES

The seeds of the water-melon described variously as *Citrullus vulgaris*, *Cucumis citrullus* and *Cucurbita citrullus* are composed of some 35 per cent. of husk and 65 per cent. of kernels of which latter about two-thirds is oil. The seeds differ somewhat in composition according to the source, thus seeds from the Sudan (*J.S.C.I.*, 1916, 35, 1024) yielded only 23·6 per cent. of oil calculated on the air-dried product, whilst Power and Salway found

* The extracted oil appears to have a lower iodine value than the expressed oil.

only 19·6 per cent. of oil. The oil is of a pale yellow colour with weak drying properties and a mellow taste.

Power and Salway found the oil to consist of the glycerides of stearic and palmitic acids (30 per cent.) oleic acid (25 per cent.) and linolic acid (45 per cent.). They found a small amount of phytosterol of M.Pt. 163°–164°. The oil does not give the Halphen or the Baudouin reactions. The characteristics of the oil are given in the following table together with those obtained by various observers on related oils. (See *Analyst*, 1925, 50, 462.)

TABLE LXXVII.—CHARACTERISTICS OF OILS FROM SEEDS OF THE CITRULLUS SPECIES

Source of Oil.	S.G. 15°.	Sap. Value.	Iodine Value.	Acid Value.	Titre. °C.	n_D^{40}.	Unsap. per cent.	Sol. Pt. °C.	R.M.
Water melon.	0·923 ..	189·7– 191·8	117·1– 121·8	2·4– 8·4	30–32	..	0·7– 1·1	..	..
[1] *Citrullus vulgaris*	0·914 0·922	194·0 198·2	106·0 123·7	1·4	32–36	1·4656	1·34	−5	..
Citrullus vulgaris	0·916– 0·923	195·6– 198·1	115·5– 124·3	1·3– 17·8	33·0– 29·2	1·4645– 1·4670	0·28– 1·1	−5 −10	..
[3] *Citrullus Colocynthis*	0·929	187– 203	120– 129	..	27– 29	1·4682	..	−14	0·3
[2] *Citrullus naudinianus*	..	203·1	120·3	..	..	1·4674	4·37	−7	..

[1] Described as "Ikpan-seed oil." Figures by Imperial Institute and Grimme. [2] Heering and Grimme. [3] Grimaldi and Prussia, A., 1910. 35, 73.

Similar oils have been described by Pieraerts (*J.S.C.I.*, 1918, 37, 741A). One described as sélé is popular among the natives of the Belgian Congo. It consists apparently of the glycerides of oleic, linolic, stearic, palmitic, and lauric acids of which the liquid glycerides predominate. This oil which is a semi-drying oil is an excellent edible oil with good keeping properties. A similar oil, known as "Cocorica," is obtained from a variety of *Citrullus vulgaris* in the Yangambi district, but the low yield and slow and difficult decortication of the seed renders this unsuitable for commercial purposes.

COUMOU OIL

This oil, also known as Coumou, Batana, or Patava oil, is obtained from the kernels of the Brazilian palm-tree, *Œnocarpus batava*. It has been described by Bolton and Hewer (*Analyst*, 1917, 42, 42) in the following

way: " The oil is prepared by the natives from the pulp, and the specimens of depericarped seeds examined by the authors were found only to contain mere traces of oil. The native prepared oil varies from a pale green to a yellowish-green colour and is almost odourless and tasteless. All the samples examined were found to be very low in acidity. The oil bears a striking resemblance to olive oil, and, save for a distinctly lower refractive index and a hardly appreciably lower iodine value, the analytical constants are strikingly similar, including its specific gravity of 0·9158. When subjected to Bellier's test, as modified by Evers (*Analyst*, 1912, 37, 488) it behaves in a similar way to olive oil."

The oil has also been examined by Grimme (*Analyst*, 1910, 35, 536). The seeds contain about 35 per cent. of oil having the following characteristics:

Specific gravity 15°	0·925
Melting-point °C.	−7·5
Saponification value	190·5, 191·8
Iodine value	80·0, 78·2
Unsaponifiable matter	0·76, 1·1 per cent.
n_D^{40}	1·4600, 1·4610
Acid value	1·4, 1·0
Melting-point of fatty acids °C.	19·5
Iodine value of fatty acids	85·3

The oil of *Œnocarpus distichus* has been examined by Bolton and Jesson (*Analyst*, 1915, 40, 8). " The fruit of this tree is a subglobose or ovate, blackish-brown berry. Beneath the outer, brittle layer is a very characteristic fibrous one enclosing the extremely hard seed. A soft brownish-green fat of lard-like consistency and low melting-point was obtained from these seeds, and was found both in the hard seed as well as in the fibrous shell." The oil had the following characteristics:

Saponification value	209·2
n_D^{40}	1·4587
Iodine value	55·0
Acid value	130·0
Unsaponifiable matter	2·15 per cent.

Garden-Cress Oil

Garden-cress oil obtained from the seeds, *Lepidium sativum*, which contain about 20 per cent. of the oil, is used to some extent as an edible oil. It is characterised by a high iodine value and a peculiar odour. The oil has been examined by various workers, notably Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 991) and Grimme (*J.S.C.I.*, 1912, 31, 500). The following characteristics have been observed by these and other workers—the oil from the seeds of the water cress (*Nasturtium officinals*) and the winter cress (*Barbarea præcox*), which have been examined by Grimme (*loc. cit.*) are added for comparison.

TABLE LXXVIII.—CHARACTERISTICS OF GARDEN-CRESS OIL

	Garden Cress.	Water Cress.	Winter Cress.
Specific gravity 15·5°	0·920–0·924	0·921	0·921
Solidifying-point	−6 to −15	−5 to −6	−5 to −7
Saponification value	181–186	170·9	180·0
Iodine value	130–140 *	98·6	137·3
Refractive index 40°	1·4645	1·4632	1·4677
Solidifying-point of fatty acids °C.	22–23	21–23	21–22
Melting-point °C.	20–26	24–25	23–24
Iodine value of fatty acids	138–145	102·5	139·2
Unsap. matter per cent.	1·23	1·11	0·98

KAPOK OIL

Kapok oil is obtained from the seeds of *Eriodendron aufractuosum*, a plant which grows in almost all tropical countries. It is very similar to the East Indian Tree, *Bombax malabaricum*, the seeds of which are also known as kapok seeds and indeed, in commerce, little if any difference is made between the two varieties. Samples of the Indian oil examined at the Imperial Institute (*Analyst*, 1921, 46, 196) were, however, found to differ somewhat from the Java oil; the figures obtained are given in the table below. The seeds of *Bombax malabaricum* usually contain somewhat more oil than those of *E. Aufractuosum*. The Mexican oils are considered to be superior in colour to those of the Java oils (S. and D., *loc. cit.*).

The tree is known as the " silk cotton tree " and even as the " cotton tree," and resembles the true cotton plant in that the seeds are embedded in a mass of fibrous material which may be used for textile purposes. (*J.S.C.I.*, 1894, 13, 147), but they are quite free from hairs and therefore do not offer the same difficulty in regard to decortication as do the latter. The wax contained in the fibre has been examined by Matthes and Streicher (*J.S.C.I.*, 1914, 33, 1215).

The seeds are about the size of peas and are black in colour, having a hard shell which constitutes about 40 per cent. of the whole. The oil content of the seeds varies from about 20 to 25 per cent., the commercial yield by hot pressing being about 18 per cent. The seeds are lightly crushed between rollers and the kernels then separated by means of sieving in a current of air.

The composition of the oil has not been studied to any great extent, but Philippe has stated that the fatty acids consist of 30 per cent. solid and 70 per cent. liquid, the solid acids consisting principally of palmitic. These figures are, however, somewhat doubtful and further examination of the oil is desirable. Matthes and Holtz (*J.S.C.I.*, 1913, 32, 917) found a small amount of phytosterol having M.Pt. 136°. The fatty acids are stated readily to yield lactones on boiling with water. (*J.S.C.I.*, 1902, 21, 1336; 1903, 22, 306; 1915, 34, 184.)

The expressed oil varies in colour from yellow to deep brown and some samples deposit a considerable amount of stearine on standing. The most striking property of the oil is that it gives the Halphen reaction even more strongly than cotton-seed oil, in fact Besson (*J.S.C.I.*, 1915, 34, 184) states

* Lower values have been given down to 101 but they would appear to be open to objection.

that the red colouration produced by kapok oil with Halphen's reagent is about twenty times more intense than that given by cotton-seed oil and that the presence of 0·05 per cent. of kapok oil in other oils may be detected by this test. The oils may be distinguished (Sprinkmeyer and Diedricks, *Analyst*, 1913, 38, 467) (cf. *Analyst*, 1903, 28, 40, 320) by means of the test devised by Milliau (*Analyst*, 1905, 30, 98) and modified by Durand and Band which is thus described by Mitchell:

15 c.c. of the oil are saponified with sodium hydroxide and alcohol in the usual manner, 200 c.c. of boiling water are added, and the whole boiled until the alcohol has evaporated. The fatty acids are then thrown out by the addition of N/10 sulphuric acid in slight excess. The fatty acids are skimmed off, and shaken twice with 15 c.c. of *cold* distilled water, the water being then drained off and the fatty acids dried rapidly in an oven at 105°. 5 c.c. of these fatty acids are shaken with 5 c.c. of a 1 per cent. solution of silver nitrate in absolute alcohol. Under these circumstances cotton-seed oil only produces a *barely perceptible brown colour*, whilst kapok oil readily develops a *deep coffee colouration*. By means of this test it is possible to recognise 1 per cent. of kapok oil in other liquid oils.

Besson (*loc. cit.*) states that the oils may be differentiated by shaking a solution of the oil in chloroform with a 2 per cent. solution of silver nitrate in absolute alcohol when kapok oil gives an almost immediate coffee-brown colouration, whilst cotton-seed oil yields a yellow colouration only after some hours. Besson claims that 1 per cent. of kapok oil may be detected in cotton-seed oil by this test, whilst as little as 0·25 per cent. of kapok oil may be detected in oils such as olive, sesamé, etc., which give no reaction by means of this test.

The following constants have been obtained by various observers. The oils from varying sources have been distinguished as far as possible.

TABLE LXXIX.—CONSTANTS OF KAPOK OIL

Observer.	Source.	S.G. 15°.	Sap. Val.	Iod. Val.	$n_D^{40°}$.	Titre. °C.	Acid Value.	R.M.	Pol.	M.Pt. Acids. °C.
[6] Sprinkmeyer and Diedrichs	*E. aufractuosum*	0·924 0·933	189·2 194·5	85·2 93·5	1·4605 1·4657	26·9– 31·8	..	..	..	..
[6] S. and D. .	*B. malabaricum*	0·930	194·3	73·6	1·4369	..	3·0	..	..	..
Matthes and Holtz	*E. aufractuosum*	[1]0·922 [2]0·920	192·3 196·3	88·7 93·3 94·5	1·4630 ..	.. ..	21·6 3·4– 4·6	0·1 ..	0·1 0·3	[4]34–36[5] ..
S. and D. . .	[3]*Bombax Species*	..	192·8	95·7	1·4642	28·0	12·6	0·6	..	31·2
[5] Imperial Institute	*B. Malabaricum*	0·921	193·3	78·0	1·4610	..	9·3	0·0	0·5	..
[4] Georgii . .	*E. aufractuosum*	0·918	191·0 193·3	94·3 98·1	..	28·4	..	..	..	..

[1] Expressed oil. *J.S.C.I.*, 1913, 32, 917. [2] Extracted oil. [3] Different from the true kapok seed. "Mexican kapok." *J.S.C.I.*, 1913, 32, 1118.

[4] Unsaponifiable matter, 0·8–1·1 per cent. This author gives the following figures for the composition of the Java seeds. (*J.S.C.I.*, 1923, 42, 462A); yield of oil from undried seed, 16·8–22·1 per cent.; yield from dried seed, 19·4–24·4 per cent.; husk, 43·2 per cent.; kernel 56·8 per cent.; oil content of kernel 40 per cent. The extracted cake contained 3·98 per cent. of nitrogen. [5] *Analyst*, 1921, 46, 196. [6] *Analyst*, 1913, 38, 467.

A sample of hardened kapok oil has been examined by Mellana (*J.S.C.I.*, 1914, 33, 701) who found that the product had M.Pt. 55°; titre, 48°; saponification value, 191; iodine value, 32; $n_D^{60°}$, 1·4538.

Lemon-Seed Oil

Lemon-seed oil is obtained from the large quantities of the seeds of the common lemon which are a by-product of the production of pickled peel, essential oil and citric acid. The seeds are roughly dried, ground and extracted as expression does not remove more than a small quantity of the oil. (Bertolo, *J.S.C.I.*, 1921, 40, 153A.) The seeds usually yield from 30 to 35 per cent. of oil; the kernels contain some 50 per cent. The expressed oil is clear, but the extracted oil is turbid, and gradually deposits considerable sediment consisting largely of solid, saponifiable substances; the oil retains a pronounced odour of lemons and a somewhat bitter taste; it has a dark yellow colour and a green fluorescence, which is not removed by repeated washing with hot water or dilute sulphuric acid.

According to Bennett (*J.S.C.I.*, 1922, 41, 639A) the oil is of a clear orange colour when obtained by cold extraction, but much darker when prepared by hot extraction.

The oil has not been examined at length but it probably consists of palmitic, stearic, oleic and linolic acids. Characteristics for the oil have been determined by various workers; these are placed in the following table. The oil is a semi-drying one which does not give the Halphen reaction.

Table LXXX.—Constants of Lemon-Seed Oil

Observer.	S.G. 15·5°.	Sap. Value.	Iodine Value.	n_D^{40}.	Acid Value.	R.M.	Pol.	Titre. °C.	M.Pt.of Acids. °C.	Sol. Pt. of Oil. °C.
[1] Peters and Frerichs .	..	188·4	109·2	..	..	..	..	..	..	..
[3] Diedrichs.	..	196	107·3	1·4659	1·8	0·6	0·3	..	..	..
[2] Bertolo .	0·921[4] 0·923[5]	190 191	103 108	1·4669	5·6	..	..	35–38	41	−5 to −6
[6] Bennett .	0·923	189	109	..	23·0	..	..	31·9	..	..

[1] *J.S.C.I.*, 1903, 22, 102. [2] *J.S.C.I.*, 1921, 40, 153A. [3] *J.S.C.I.*, 1914, 33, 1098. [4] Expressed oil. [5] Extracted oil. [6] *J.S.C.I.*, 1922, 41, 639A.

The composition of lemon peel and lemon seeds has been investigated by Mach and Lederle (*J.S.C.I.*, 1918, 37, 105A)—the figures obtained by

this worker together with those obtained for the similar product of the orange are given in the following table:

TABLE LXXXI.—COMPOSITION OF ORANGE AND LEMON PEEL AND SEEDS (MACK AND LEDERLE)

	Water.	Crude Protein.	Crude Fat.	Nitrogen-free Extractives.	Crude Fibre.	Ash.
	%	%	%	%	%	%
Orange peel . . .	19·30	4·66	1·92	62·67	8·12	3·33
Lemon peel . . .	14·03	7·01	1·56	61·16	11·80	4·44
Lemon peel . . .	15·32	6·56	2·17	56·66	14·00	5·29
Orange pips . . .	6·82	13·72	33·37	31·22	11·30	3·57
Lemon pips . . .	8·23	18·25	34·30	22·21	14·35	2·66

MAIZE OIL

Source.—Maize oil (largely described as corn oil in the United States and elsewhere) is obtained from the seed of the maize plant, *Zea mays*. Practically the whole of the oil is contained in the germs (which contain more than 20 per cent. of oil) which are by-products in the manufacture of maize starch and glucose syrup. These are the main source of the oil, although a certain proportion is still obtained from the fermentation vats in the manufacture of alcohol where the oil rises to the top and may be ladled off before distillation of the alcohol. This fermentation oil, however, is usually very dark and has a very high acid value with characteristics different from the oil obtained by expression. Edible oils are obtained entirely by expression. Lewkowitsch states that the dry germs contain 53 per cent. of oil, but this is the amount of oil in the completely separated germ, and other writers using the commercially separated material give considerably lower results. (Cf. Wagner, *J.S.C.I.*, 1909, 28, 342). The germs are separated by mechanical means and then pressed in a hydraulic press in the usual way. (Cf. *J.S.C.I.*, 1921, 40, 192A, 823A). Sievers and Shrader (*J.S.C.I.*, 1922, 41, 473A) have given methods for the production of an edible oil from the crude oil, whilst Thurman (*J.S.C.I.*, 1923, 42, 561A) gives an account of the losses taking place during refining.

Sievers (*J.S.C.I.*, 1922, 41, 507A) has carried out an investigation on the comparison of the oils obtained by expression and benzol extraction, the extraction method being used both on the germs themselves and on the press-cake. He found that there were no striking differences in the physical and chemical constants of the oils from the two types of germs by the two different methods of extraction. No material difference could be noted in the finished oils from the germs immediately after their preparation, but upon standing, some deterioration took place, and this was more noticeable in the extracted oils than in the expressed oils. All oils were sufficiently light in colour for use as salad oils and for cooking purposes. The oils obtained by benzol extraction of the two types of oil cake were inferior in all respects to the oils from the germs, that from the cake from the wet-process germs being the poorer of the two.

Composition.—The composition of maize oil has not been dealt with by

more than a few workers. Lewkowitsch states that the unsaturated acids consist of a mixture of oleic and linolic acid and quotes Vulté and Gibsen as stating that the saturated acids consist of palmitic, stearic, and arachidic acids. Hehner and Mitchell (*Analyst*, 1896, 21, 328) did not detect stearic acid by their method. Leathes (*The Fats*, London 1910, p. 15) reports the presence of hypogæic acid in the oil.

The composition has been thoroughly dealt with recently by Baughman and Jamieson (*Analyst*, 1922, 47, 171), who find for a sample of expressed oil the following composition:

	Acid.	Per Cent.
Glycerides of	Oleic	45·4
	Linolic	40·9
	Palmitic	7·7
	Stearic	3·5
	Arachidic	0·4
	Lignoceric	0·2
	Unsap. matter	1·7
		99·8

At one time it was considered that maize oil offered a distinction from other vegetable oils in that the unsaponifiable matter contained cholesterol. Gill and Tufts, however (*J.A.C.S.*, 1903, 25, 251) found that the sterol had M.Pt. 138° and that the acetate had M.Pt. 127°. König and Schluckebien found these M.Pts. to be 140·4° and 137° respectively, whilst Steuart (*Analyst*, 1923, 48, 158) found that the crude acetate had M.Pt. 130° which fell to 119° after the third crystallisation. This last observation throws more than doubt on the utility of the suggestion of Gill and Tufts to use the M.Pt. of the acetate as a means of detecting maize oil in cotton-seed oil, the phytosteryl acetate of the latter having M.Pt. 121° (Steuart found 125·5°—122·5°—122·5°—118·5° in successive crystallisations). Anderson and Moore (*Analyst*, 1923, 48, 556) find that the sterol is a homogeneous substance, identical with sitosterol and free from stigmasterol, with M.Pt. 137·5°, $[\alpha]_D^{20}$ −34·34°, and forming an acetate with M.Pt. 127°. Anderson in a later paper (*Analyst*, 1924, 49, 399) finds that the unsaponifiable matter from the endosperm of maize contains at least two sterols. He confirms the presence of free phytosterol with M.Pt. 137·5° $[\alpha]_D^{20}$ −32·2 forming an acetate with M.Pt. 127°, but finds further that after saponification the unsaponifiable matter may be divided into three parts: (1) optically active dihydrositosterol, $C_{27}H_{47}OH{\cdot}H_2O$ (M.Pt. 138–139) which when dried had M.Pt. 140°–141°, $[\alpha]_D^{20}$ +25° and formed an acetate with M.Pt. 138° and $[\alpha]_D^{20}$ +14·41°; (2) The ordinary sitosterol; and (3) a brownish-yellow oily substance which was not further examined.

It seems most probable that the different results so far obtained when working on the sterols of maize oil may be due to the extraction of varying proportions of phytosterol and sitosterol by variations in the method of preparing the oil. The subject is in need of extended investigation. These later investigations throw considerable doubt upon the statement of M'Pherson and Ruth (*Analyst*, 1907, 32, 329) that the phytosteryl acetate test will detect as little as 2 per cent. of maize oil in lard.

Maize oil contains 1·1 to 1·5 per cent. of lecithin.

TABLE LXXXII.—ANALYTICAL CHARACTERISTICS OF MAIZE OIL (VARIOUS OBSERVERS)

Observer.	S.G. 15°.	Sol. Pt. °C.	Sap. Value.	Iodine Value.	R.M.	n_D^{40}.	Acid Value.	Titre. °C.	Unsap. per cent.
Mitchell .	0·921–0·927	−10 to −12	186–193	115–128	4–4·5 *	..	..	..	1·4–1·7
Leach . .	0·921–0·926	..	188–193	111–130	4–5 *	1·4673	1·3–2·9	..	1·7–2·1
Fryer and Weston .	0·921–0·927	..	190–193	115–125	..	1·4655–1·4663	6	18–19	1·5
Lewkowitsch	0·927	..	191·9	121–130·8	..	1·4678	..	19	1·35–2·32

Rabak (*Analyst*, 1920, 45, 101) has examined the effect of mould, growing upon maize, upon the characteristics of the oil. The maize was inoculated with *Penicillium* and samples were taken at intervals during a period of ninety days. The results of the examination of the oils obtained from the various samples are given in the following table, No. 1 representing the original sample and No. 5 that after the ninety days.

TABLE LXXXIII.—ANALYSIS OF MAIZE INOCULATED WITH *Penicillium*

	Yield per cent.	Acid Value.	Sapon. Value.	Iodine Value.	R.M.	Sol. Acids.	Insol. Acids.	Acetyl Value.	Unsap. Matter per cent.
1 . .	5·58	13·6	190·3	121·0	12·8	1·3	93·6	15·3	4·13
2 . .	4·33	46·7	191·7	121·3	2·95	1·5	90·5	10·6	9·9
3 . .	2·67	84·6	192·4	120·4	2·23	3·28	92·3	61·1	10·8
4 . .	2·06	68·7	185·1	119·0	2·92	2·35	91·7	28·4	15·3
5 . .	2·02	72·1	126·6	96·6	..	4·05	..	68·4	25·4

It is somewhat difficult to see why such a large fall in the Reichert value causes a considerable increase in the percentage of soluble acids, it seems likely that " 12·8 " should read " 1·28," but even so the Reichert figures and the soluble acid figures are difficult to reconcile.

Properties and Special Tests.—The oil is of a bright golden yellow colour having a distinctive odour and flavour of grain. On account of this somewhat aggressive flavour it is frequently mixed with cotton-seed and other seed oils when used as a salad oil. The oil is of the semi-drying type having somewhat better drying properties than cotton-seed oil (Archbutt, *J.S.C.I.*, 1899, 18, 346).

No special tests have been described for the oil which gives no reactions with Halphen's of Baudouin's tests, whilst the presence of cotton-seed oil will increase the titre. The oil gives no precipitate in the insoluble bromide test.

* Old figures obtained from " fermentation " oil. The pressed oil gives an almost negligible figure.

Maize oil has been used from time to time for the adulteration of other oils. For its detection the iodine value may be of some assistance, whilst the presence of lecithin, as shown by a high proportion of alcohol soluble phosphorus, would be, in the absence of other lecithin containing substances, confirmatory evidence. The hydrogenation of maize oil has been discussed by Reichert and Trelles (*J.S.C.I.*, 1921, 40, 551A).

Melon-Seed Oil

Melon-seed oil is obtained from the seeds of *Cucumis melo*, which are used for edible purposes on parts of the West Coast of Africa. The oil is also known as Cantaloup-seed oil. Lewkowitsch quotes some results by Lidoff on a melon-seed oil which is obtained by expression and which is used as an edible oil in South Russia with the suggestion that they appear unreliable. The seeds contain about 40 per cent. of oil.

The composition of the oil has been studied by Baughman and his co-workers (*Analyst*, 1921, 46, 51), who consider that the oil * is composed of myristin 0·3, palmitin 10·2, stearin 4·5, olein 27·2, linolin 56·6 and unsaponifiable matter 1·1. The oil gives no deposit in the insoluble bromide test and belongs to the semi-drying class. Characteristics obtained by various workers are contained in the following table which also includes some figures obtained by the Imperial Institute on the oil of *Cucumis chate* and some by Hopper on that of *Cucumis sativus* as well as the figures obtained for *C. melo* by Lidoff.

Table LXXXIV.—Characteristics of Melon-Seed Oil

Source.	Authority.	S.G. 15°.	Sap. Value.	Iodine Value.	Acid Value.	Reichert.	Titre. °C.
C. melo . . .	Fendler †	..	193·3	101·5	..	..	36
	Baughman	0·927	192·3	125·9	0·4	0·3	..
	Lidoff	0·928	190·5	133·3	1·4	..	..
C. Chate . .	Imperial Institute	0·924	187–192	117–128·5	..	..	30·3
C. sativus . .	Hooper	0·924	195·2	117·6	11·5	0·5	35·5
		0·923	196·9	118·5	11·5	0·5	

Black Mustard-Seed Oil

Black mustard-seed oil is obtained from the seeds of *Sinapis nigra*. The oil closely resembles white mustard-seed oil (obtained from the seeds of *Sinapis alba*) and colza oil in composition but both mustard-seed oils are distinguished from colza by the pungent odour of volatile oil of mustard. Mustard-seed oil is used for burning and lubricating, but in India the highly-refined oil is used for edible purposes. The oils have been examined by

* Acetyl value 15·8, Polenske 0·3, unsapon. matter 1·1 per cent., n_D^{40} 1·4652.
† Sol. Pt. 5·5°. M.Pt. 5°.

Blasdale (*J.S.C.I.*, 1896, 15, 206), Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 992), Grimme (*J.S.C.I.*, 1912, 31, 997), Huber and Van der Wielen (*J.S.C.I.*, 1915, 34, 1259), Raynes (*Analyst*, 1918, 43, 216), and other workers. The characteristics given in the following tables are taken from these results—the figures of Huber and Van der Wieber are of sufficient interest to give their table complete, which is as follows :

TABLE LXXXV.—CHARACTERISTICS OF BLACK MUSTARD-SEED OIL

Origin of Seed.	No. of Seeds in 1 grm.	Volatile Oil per cent.	Fatty Oil per cent.	Sp. Gr. 15°.	Ref. Ind. 22°.	Iodine Value.	Sap. Value.
Dutch . . .	1125	1·23	25·7	0·923	1·4731	126	183
North Holland .	976	1·15	28·0	0·921	1·4724	124	187
English . . .	630	1·07	31·4	0·920	1·4719	119	182
Russian . . .	362	0·63	37·0	0·921	1·4725	120	189
Caucasian . .	1690	1·07	29·8	0·919	1·4712	113·5	190
Italian . . .	910	0·87	32·5	0·919	1·4720	115	188·5
Sicilian . . .	964	0·94	32·9	0·921	1·4721	114·5	187
Rumanian . .	490	0·66	35·7	0·921	1·4714	120	190
Bombay . . .	292	1·07	33·5	0·920	1·4721	119	183

	Black Mustard Seed.	White Mustard Seed.
Specific gravity 15·5° . . .	0·916–0·920	0·912–0·917
Solidifying-point °C. . . .	−15	−16
Saponification value . . .	174–180 *	171–178
Iodine value	115–126 †	98–108
n_D^{40}	1·4655–1·4670	1·4650–1·4660
Titre °C.	6–8	9–10
Iodine value of fatty acids .	115–120	110
Iodine value of liquid fatty acids	120	103

ORANGE-SEED OIL

Orange-seed oil is obtained from the seeds of the common orange, *Citrus aurantium*. They may be obtained as a residue in the dried peel and essential oil industry and also from the manufacture of marmalade. The seeds consist of about 55 to 60 per cent. of oil. The oil differs to a certain extent in its physical properties according to its age, a sample examined by Hewer (*Analyst*, 1917, 42, 271) being clear and almost odourless and tasteless (the bitter flavour increased rapidly on keeping), whilst Brewis found that a sample had a strong odour of the essential oil. For the composition of orange seeds and peel see under Lemon-Seed Oil, page 204. For details of the Osage orange (*Maclura pomiferum*) see *J.S.C.I.*, 1914, 33, 544; 1915, 34, 840.

* Cf. the figures of Huber and Van der Wielen.
† Earlier observers gave much lower results 96–110.

The following characteristics have been observed:

TABLE LXXXVI.—CHARACTERISTICS OF ORANGE-SEED OIL

Observer.	S.G.	Sap. Value.	Iodine Value.	n_D^{40}.	Titre.	M.Pt. Acids.	Acid Value.	Unsap. per cent.	Iodine Value of Acids.
[1] Meyer . .	0·923	229	104	1·4638	35	40	38·3	..	..
[2] Diedrichs .	0·925	196·4	..	1·4642	34	39·5	0·5	..	100·4
[3] Hewer . .	0·921	193·7	100·3	1·4643	34	..	0·6	..	..
[3] Brewis . .	0·922	194·6	97·8	1·4645	..	..	..	..	..
[4] Kobayashi .	[5] 0·922 [6] 0·920	195·1 192·7	100·4 105·3	1·4647 1·4649	29–30 34	34 40–41	5·0 0·9	1·28 1·22	102·4 105·9

[1] *Chem. Zeit*, 1903, 27, 958. [2] *J.S.C.I.*, 1914, 33, 1098. [3] *Analyst*, 1917, 42, 271. [4] *J.S.C.I.*, 1919, 38, 294A. [5] *Citrus aurantium*, L. sub. sp. *junos*. Mak. The Citron. [6] *C. aurantium* L. sub. sp. *sinensis* Engl. The Chinese citron.

PECAN OIL

Pecan oil is obtained from the pecan nuts, *Juglans nigra*, which are cultivated in North America for edible purposes. The nuts, according to Deiler and Fraps (*Analyst*, 1910, 35, 134), contain 47 per cent. of kernels, which latter yield 70 per cent. of oil to ether. The oil is stated to be of a light straw colour having a pleasant odour and taste and somewhat closely resembling olive oil. It is a non-drying oil containing, it is stated (D. and F.), no saturated acids. The following characteristics were determined:

Specific gravity at 15°	0·9184
Saponification value	198·0
Hübl's iodine value	106·0
Volatile acids (Reichert-Meissl)	2·2
Acetyl value	1·16
Insoluble fatty acids	93·4 per cent.
Lecithin	0·5 ,,
Cholesterol	0·28 ,,

The nut *Juglans sieboldiana* has been examined by S. Higuchi (*J.S.C.I.*, 1916, 35, 262), who found that the kernels contained 62 per cent. of oil. He describes the oil as colourless having a slight agreeable smell and taste. It is a drying oil and is used for white paint by artists. The oil, which is known as onigurumi oil, was found to have the following characteristics:

Specific gravity at 15°	0·928
Acid value	0·5
Saponification value	187·5
Iodine value	153·7
Reichert value	4·9
M.Pt. of fatty acids °C.	28
Iodine value of fatty acids	150·6 (cf. Walnut Oil, page 186).

Pumpkin-Seed Oil

This oil is obtained from the seeds of the pumpkin, *Cucurbita pepo*, which grows freely in all warm climates. Of the whole fruit the seeds and rind consist of about 60 per cent. of the whole. The seeds consist of about 25 per cent. husk and 75 per cent. kernels. The oil content of the seeds is somewhat variable, figures as low as 25 per cent. having been found, but as a rule the percentage of oil in the seeds is about 35, whilst that in the kernels is about 45.

The seeds as usually obtained are wet and must first be dried thoroughly, which drying may have some effect on the constants of the oil. In some cases the dried seeds are crushed and extracted with, say, petroleum spirit (*J.S.C.I.*, 1918, 37, 474A), when about 40 per cent. (on the dry seeds) of a green oil is obtained. Edible oils are better obtained by pressing in the cold when a green oil is obtained, having a pleasant odour and taste.

The composition of the oil has been studied by Power and Salway who found the oil to consist of the glycerides of linolic acid (45 per cent.), oleic acid (25 per cent.), and palmitic and stearic acids (30 per cent.). They found small quantities of a phytosterol which melted at 162°–163° and another which melted at 140°.

The oil is said to be frequently adulterated with linseed, cotton seed, sesamé and rape oils. The most useful tests to apply would be iodine value, Halphen and Baudouin tests, and possibly saponification value. The oil gives no precipitate in the insoluble bromide test. The oil has the following average constants:

Specific gravity 15°	0·920–0·925
Solidifying-point °C.	−16
Saponification value	188–190·5
Iodine value	120–130
n_D^{40}	1·4668–1·4685

The oil from the Indian pumpkin and that from the Indian squashed gourd (*Cucurbita maxima*) have been examined by Hooper; he obtained the following results:

	Pumpkin.	Gourd.
S.G. 15°	0·926–0·928	0·926
Sap. value	195·7–196·2	197·1
Iodine value	126·0–129·6	133·4
Reichert value	0·4–0·5	0·7
Titre test °C.	31–32	38

Tomato-Seed Oil

Tomato-seed oil is obtained from the seeds of the tomato plant, *Lycopersicum esculentum*, Mull., which are a waste product of the tomato canning industry in Italy and the United States. Accomazzo (*J.S.C.I.*, 1911, 30, 95) states that in the province of Parma in Italy in 1908, 3000 tons of the dried seeds were available, which yield 18 per cent. of oil on cold pressing and 20 per cent. by extraction. (Cf. Shrader, *J.S.C.I.*, 1920, 39, 131A, who states that the seeds amount to about 0·5 per cent. of the fruit.)

Rabak (*J.S.C.I.*, 1918, 37, 70A) in a long report to the U.S. Department of Agriculture states that in the preparation of tomato pulp the fresh tomatoes are washed by a stream of water under pressure, then cooked with steam, and pulped in a cyclone machine which separates the seeds and skins; or a cold process is used in which, after removal of the 'culls' the washed tomatoes pass directly to the cyclone machine. It is estimated that in the

U.S.A. about 300,000 tons of tomatoes are annually pulped, and that the moist waste amounts to about 16,000 tons, corresponding to approximately 3300 tons of dry waste, yielding about 1500 tons of dry seeds and 1800 tons of dry skins. This estimate is based upon the data that American tomatoes yield on the average 0·52 per cent. of dry seeds and 0·61 per cent of dry skins. In Italy the wet seed and skins are pressed and then dried in a desiccating machine heated by means of steam pipes and containing horizontal conveyors. About 10 tons of the residue is dried in 24 hours, and the seeds are then separated from the skins in a machine containing a series of sieves and fans. The yield of oil from the seeds by extraction with ether or carbon tetrachloride is about 22 per cent. of the ground seeds. The extracted oil contains more impurities than the expressed oil, and in the crude state has a slightly rancid odour and a slightly bitter taste, but it can be readily deodorised by the action of steam, and to a large extent decolorised by treatment with Fuller's earth and filtration. Under the present conditions about 343 tons per annum of tomato-seed oil would be available in the United States. Experiments have shown that the oil has a digestibility value of 97, which compares favourably with the value of olive, almond and cotton-seed oils. It would be useful as a culinary and salad oil and would probably yield a satisfactory hydrogenation product for margarine. By cold saponification with caustic soda it yields a soap of good texture with excellent lathering properties.

The oil is of a pale yellow colour having a pleasant nutlike odour and taste. It has pronounced drying properties of the order of those of cotton-seed oil. The composition of the oil has been studied by several workers. Battaglia found the fatty acids to consist of myristic, stearic, oleic and linolic acids whilst Rabak (*loc. cit.*) found palmitic but not apparently myristic. Jamieson and Bailey (*Analyst*, 1919, 44, 373) state that the Renard test indicates the presence of a quantity of arachidic acid, but that they were only able actually to isolate 0·4 per cent.

The following characteristics have been observed by various workers:

TABLE LXXXVII.—CHARACTERISTICS OF TOMATO-SEED OIL

Observer.	S.G. 15°.	Sap. Val.	Iodine Val.	Sol. Pt. °C.	Reichert.	n_D^{40}.
[1] Kochs	0·920	183·6	117·8	−9 to −12	0·2	1·4678
[2] Battaglia . . .	0·922	190·4	106·9	..	..	1·4675
Accomazzo . . .	0·920	184	118	..	..	..
[4] Rabak	[3] 0·924	188·6	114·2	−10	..	1·4661
[5] Jamieson and Bailey.	0·924 0·925	187·0– 192·0	117·5 125·0	..	[6] 0·1 to 0·3	..

[1] *Analyst*, 1908, 33, 423. M.Pt. of fatty acids 26–29, unsaponifiable matter 2·68 per cent. [2] *Ann. Chem. Anal.*, 1901, 6, 437. [3] Calculated from 0·9184 at 24°. [4] Iodine value of liquid acids 130, acid value 2·5, titre 20·5–21·5. [5] Nine samples of U.S. oil. [6] Polenske 0·4–0·6; acetyl value 10·0–20·5.

CHAPTER XIII

Cotton-Seed Oil

Source.—Cotton-seed oil is obtained from the seeds of various varieties of the cotton tree, *Gossypium*. There is some confusion in regard to the botanical classification of the different varieties, but it is generally conceded that American " Upland " cotton is derived from *G. herbacecum* or *G. hirsutum*, which are considered by many observers to be synonymous. " Sea Island " cotton is probably derived from *G. barbadense*. Egyptian cotton is obtained from various varieties of *G. barbadense*. Indian cotton is probably derived from *G. arboreum* and *G. herbacecum* (with possibly some others) whilst Southern American cottons are derived from *G. brasiliense* (Brazil) and *G. peruvianum* (Peru).

Cotton-seed oil is expressed and used in large quantities in several European countries, but in some ways the oil may be looked upon as typical American. The following extract from *Some American Vegetable Food Oils*, by H. S. Bailey, will show how important the oil is in the United States: " From the data in Tables 1 and 2 it is apparent that the United States produces more cotton-seed oil than any other single oil—nearly 1,344,000,000 pounds during the calendar year 1917. We likewise consume more of this oil than of all other vegetable oils combined. This is due not only to its suitability for both table and cooking purposes, but also to the fact that it forms the bulk of the lard substitutes, and that large amounts are employed in the manufacture of oleo-margarine, as well as in soap and other technical industries."

Some idea of the far-reaching importance of the oil will be gathered from the accompanying diagram taken from *The Chemical Age* (1925, 13, 491).

As a result of this importance and, to an even greater extent, as a result of the realisation of the importance by Government Departments and individual firms, the oil has received a tremendous amount of attention at the hands of American workers, particularly of recent years; this work will be noticed below as occasion requires. The seeds used in America are mostly home-grown, whilst those used in this country are obtained from Egypt and India, the latter source of supply, although of much more recent date, now occupying an important position.

Although the seed oil had been successfully expressed in 1847 it was not until 1870 that the importance of the oil was realised and large commercial preparation undertaken. The industry now is widespread and is of the greatest importance. Of recent years two papers have dealt with the cotton-seed industry in a general sense, the first by Vakil (*J.S.C.I.*, 1917, 36, 685), which deals principally with Indian methods, and the second by De Segundo (*J.S.C.I.*, 1918, 37, 118T), who deals largely with American practice; these papers should be consulted by all interested in the subject.

Apart from the long cotton fibres which are, of course, always removed from the seeds before use, the larger proportion of the seeds obtained is covered with a layer of short cotton fibres known as " fuzzy," whilst some seeds (less than 10 per cent. of the total production) are free from this secondary growth and are known as " black " or " bald." The composition of cotton-seeds has been dealt with by many observers, all of whom state

COTTON SEED.
MEATS.
HULLS.
LINTERS.
CRUDE OIL.
CAKE AND MEAL.
FIBRE.
BRAN.
FUEL.
FERTILIZER.
CELLULOSE.
CATTLE FEED.
FOOTS.
PUTTY.
REFINED OIL.
DYESTUFFS.
FERTILIZER.
PAPER STOCK.
CELLULOSE.
BASIS FOR EXPLOSIVES.
WRITING PAPER.
GUNCOTTON NITRO-CELLULOSE OR PYROCELLULOSE.
PRESSED PAPER PRODUCTS.
USED SAME AS UNDER LINTERS.
SOAP.
ACIDULATED FOOTS OR BLACK GREASE.
WASHING POWDER.
OFF-GRADE SUMMER YELLOW OIL.
PRIME SUMMER YELLOW OIL.
HYDROGENATED OIL.
BLEACHED OR DEODORIZED OIL.
COSMETICS.
PYROXLYN.
SMOKELESS POWDER.
FAT ACIDS.
GLYCERIN.
NITRO-GLYCERIN.
HYDRO-GENATED OIL.
MINERS' SOAP.
DEODOR-IZED OIL.
SUBSTITUTE FOR SWEET OIL.
EMULSION FOR MEDICAL PURPOSES.
COLD PRESSED OIL.
SYNTHETIC STEARIN.
LARD SUBSTITUTES.
SALAD OIL.
COOKING OIL.
ANIMAL COMPOUND LARD.
PLASTICS.
VARNISHES.
DISTILLED FAT ACIDS.
CANDLE PITCH.
SYNTHETIC STEARIN.
SOAP.
STEARIN.
WINTER OIL.
VEGETABLE COMPOUND LARD.
PHOTO-GRAPHIC FILMS.
ARTIFICIAL SILK.
VARNISHES.
COLLODION.
CELLULOID.
WATER-PROOFING
ARTIFICIAL LEATHER.
COATING FOR METALS.
OLEIC ACID.
STEARIN PITCH OR COTTON OIL PITCH
SOAP.
WASHING POWDER.
STEARIC ACID.
OLEOMARGARIN.
WINTER PACKING SARDINES.
SETTING OLIVES.
SALAD OIL.
WHITE OIL.
CANDLES.
FULLING WARE.
WASHING SOAP, POWDER.
ARTIFICIAL LEATHER.
COTTON RUBBER.
CHEAP-PAINT PROOFING.
WATER-PROOFING.
OIL-CLOTH.
INSULATING MATERIALS.
LINO-LEUMS.
ROOFING TAR.
COMPOSITION ROOFING.
BOOK BINDING.
LIPMOL-STERINE.

that wide variations in the seeds are commonly found, thus Vakil (*loc. cit.*) states that: "I find that no two samples of seeds are alike. Seeds from the same district, from the same ginning factory, even from the same field, have differed so widely that to attempt to draw any general conclusion from the analysis of a few samples would be entirely incorrect and misleading. A very large number of analyses are recorded by Mollison in the *Agricultural Ledger*, *No.* 9, 1903, published by the Department of Agriculture of the Central Provinces, and in Noel-Paton's *Indian Cotton Seeds*, published by the Government of India. The figures given there are fairly accurate, and may safely be taken as representing the average composition of Indian seeds. The following typical analyses which I have made give a general idea of the average composition of Indian seeds":

TABLE LXXXVIII.—COMPOSITION OF INDIAN COTTON-SEEDS (VAKIL)

	Oil.	Meal ex. Oil.	Husks and Lint.	Sound Seeds.
	Per cent.	Per cent.	Per cent.	Per cent.
Amalner	20·17	35·33	44·50	87·40
Yeotmal	19·64	36·66	43·70	84·50
Nagpur (Platt's gin)	20·03	35·47	44·50	96·00
Akola	22·98	34·02	43·00	94·60
Hingenghat I	18·80	38·19	43·00	90·00
„ II	19·62	35·53	44·85	89·00
Warora	18·98	37·02	44·00	92·35
Wardha	19·00	41·00	40·00	92·75
Chanda (Platt's gin)	19·13	27·37	53·50	97·25
Pandher Kavda	18·36	26·19	55·45	95·85
Average	19·67	34·68	45·65	91·77

Lewkowitsch has determined the oil in seeds obtained from various localities with the following results:

TABLE LXXXIX.—COMPOSITION OF COTTON-SEEDS (LEWKOWITSCH)

Kind of Seed.	Kernels.	Rusks.	Oil from		
			Whole Seed.	Kernels.	Husks ("Hulls").
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Maranhao I.	58·8	41·2	21·54	36·0	0·9
„ II.	59·8	40·2	20·89	34·7	0·4
Coromandel	..	..	16	..	..
Egyptian (1899)	60·0	40·0	21·98	37·41	..
„ (1900)	60·06	40·2	23·93	38·7	0·67
Mersyne	44·4	54·8	18·67	37·44	1·2
Bombay *	51·0	49·0	20·56	39·28	1·08
American Upland	..	..	23·46	..	..
Jamaica	60·0	40·0	23·6	39·3	0·37
Peru	..	..	..	35·2	..

* This is somewhat high; the average percentage of Bombay seed is nearer 18 per cent.

The content of the oil in American seeds has been found by Sievers (*J.O.F.I.*, 1924, 1, 56) to vary from 18·6 per cent. to 27·8 per cent. and this author finds some relationship between the oil content and the ammonia content.

The oil is usually expressed in presses of the normal type. British practice in general is to crush the seed whole, which tends to a dark crude oil which needs more care and trouble in refining, and for which there would seem to be no compensating advantages. The general American practice is to " decorticate " the seeds before pressing them. The removal of the hulls or " decortication " is carried out in an apparatus known as a " huller " which consists in principle of a drum containing revolving knives placed at such a distance apart that the seed coats are cut open without damage to the kernel, which thereby escapes. The hulls become coagulated together by means of the fuzzy and the mixture is passed to a sieve through which the kernels pass. American seeds have, of recent years, been less successfully decorticated on account of the improved efficiency of the de-linting machines (i.e. machines for removing the short cotton fibre before decorticating). A newer type of press has been used in America known as the propeller press. This has been described by Bailey (*U.S. Dept. of Agri., Bureau of Chemistry, Bulletin No.* 769) in the following way: " An increasing amount of crude cotton-seed oil is made in mills equipped with a type of continuous working press known as the expeller. The expeller is built somewhat on the principle of an ordinary meat-grinder, and is simply an interrupted screw, revolving inside a slotted steel barrel. The ground seed enters through a hopper at one end of the barrel, is pressed along toward the opposite end, and finally discharged around a cone which can be set in or out of the outlet orifice to give any desired pressure. Squeezed from the seed by the pressure of the screw, the oil runs out through the small slits in the barrel, and, after settling, or better, filtering through a filter-press, is ready for shipment to the refinery."

The amount of oil left in the cake is usually about 5 per cent. or sometimes less, figures below 4 per cent. having been quoted, but in decorticated cake the percentage may rise as high as 10, although usually it is lower, approximating 6 to 7 per cent. The relative feeding advantages of undecorticated and decorticated cake are to a certain extent a matter of opinion, but de Segundo states that the presence of shell in the undecorticated cake imparts astringent and other properties to the cake which are not without certain advantages, particularly in the feeding of milch cows at certain times of the year, but this circumstance can, at best, only be urged in extenuation of the British system, not in praise of it. On the improved American system the defibrated hulls are recovered as a separate product and can, together with other suitable ingredients, be compounded with the kernel-remains of cotton or other seed to produce a balanced ration. The " compounding " of the kernel-remains with the shell and other substances entails of course some additional expense, but apart from the better price such " balanced feed " should command, the cost of grinding and mixing should be more than offset by the profit on the short cotton fibres recovered from the decorticated hulls of woolly seed, not to speak of the increased value as a roughener.

The amount of refining to which it is necessary to submit the crude oil depends in great measure upon the source and freshness of the seed and also on whether the whole seed has been crushed or merely the kernels. English expressed crude oil being obtained as a rule from undecorticated seed is very dark (sometimes almost black) in colour, and considerable loss is entailed

during refining. The following remarks on crude oils by Vakil usefully point out some of the many differences likely to be found: " There is a very marked difference between the hulls of Indian and Egyptian seeds. The former contains a brown colouring matter easily extracted with water, and on this property and the behaviour of this colouring matter with sodium hydroxide and nitric acid a means of detecting the presence of Indian seed hulls in Egyptian cakes has been suggested (*Oil and Colour Trades Journal*, 1905, 1815). The chief points of difference in the crude oils obtained from these different seeds are: (1) There is a higher percentage of free fatty acid, colouring and albuminous matters in the Indian oil than in the Egyptian or American oils, which gives rise to a greater loss in refining, sometimes exceeding from 16 to 20 per cent. (2) The oil from Indian seeds is poorer than American and Egyptian oils in the solid " stearin " obtainable from it, and not quite so well suited for margarine making. Egyptian and Indian oils are inferior in colour to American oils. (3) The oil from Indian seeds retains a peculiar fishy odour which it is very difficult to get rid of even with drastic treatment. (4) The greatest drawback to the oil from Indian seeds as an edible oil is that the refined oil shows a bluish-green fluorescence. This fluorescence is not removed by the ordinary process of refining. If the traces of fishy odour and the fluorescence could be removed easily and at small cost the oil would find a ready market in India as an edible oil. At present, though sold in large quantities as edible oil, it does not command as high a price and is not valued so much as the best grades of cold-pressed Til oil. (5) The refined oil from the Indian seeds has a higher iodine value —112 to 116—than the oil from Egyptian seeds, which varies from 106 to 108, or the American, which varies from 105 to 110. This higher iodine value may be due to the fluorescent substance in the oil."

According to Sutcliffe the free fatty acids are not *always* higher in the Indian oils than in the Egyptian. Loss on refining, however, is generally greater for oils that are in any other way comparable. The Indian oil does not always give fluorescence if properly refined. One can get this fluorescence in Egyptian oils and sometimes in arachis oils by certain methods of refining. The " common edible " grade is apt to taste rather more fusty or straw-like than the Egyptian, but it can be deodorised to a normal grade just as well as the other.

The usual process used in refining cotton-seed oil is intimately to mix the warmed oil (about 120° F.) with a dilute solution of caustic soda. The caustic soda combines with the free fatty acids present and causes the precipitation of the colouring matter, which can then be removed along with the soap stock by allowing the mixture to stand and decanting the upper layer. The refining oil may then be treated with fuller's earth or some other process for bleaching and deodorisation. The bleaching of cotton-seed oil has been studied by Vilbrandt and Bankstoin (*J.O.F.I.*, 1924, 1, 71). The loss in refining under the best conditions has been stated by Thurman (*J.S.C.I.*, 1923, 42, 561A) to be about 2·27 per cent., but this represents a very high efficiency when working on the highest class crude oil prepared from decorticated cake. It may rise as high as 10–15 per cent.

Composition.—The fatty acids of cotton-seed oil are roughly in the proportion of three of liquid acids to one of solid acids. The solid fatty acids consist for the most part of palmitic acid, whilst the liquid acids probably consist of oleic and linolic only as no reaction is obtained with the insoluble bromide value when working on the oil. Meyer (Lew., Vol. II, page 199) has examined the oil by the method of alcoholysis (page 51), and his results given in the following table bear out the composition given above:

TABLE XC.—EXAMINATION OF COTTON-SEED OIL BY ALCOHOLYSIS (MEYER)

Fraction.	Boiling Point. °C.	Pressure.	Quantity obtained from 535 grms. of oil.	Iodine Value.
		mm.	Grms.	
I	up to 201·5	16	8	77·13
II	201·5–204	16	9	101·19
III	204–207·5	16	20	123·51
IV	207·5–210·5	16	83	130·87
V	210·5–214·5	16	11	123·83
VI	above 214·5	16	2	107·23

Hazura found that the proportion of oleic to linolic acids was as 3 is to 4·5, whilst Farnsteiner found quantities of linolic acid varying from 18 to 24 per cent.; these quantities are seriously low.

Jamieson and Baughman (*Analyst*, 1920, 45, 303), in an extended examination of the oil, found the fatty acids to consist of myristic 0·3; palmitic 20; stearic 2; arachidic 0·6; oleic 35·2; linolic 41·7, whilst Myddleton and Barry (*Fats: Natural and Synthetic*) found, in a sample of the oil having an iodine value of 105·4, that the fatty acids consisted of palmitic 23·4; oleic 31·6; linolic 45·0. Hilditch and Moore (*J.S.C.I.*, 1923, 42, 15T) found 24·7 per cent. of solid acids, 23·8 per cent. of oleic acid and 51·5 per cent. of linolic acid. It follows, therefore, that the fatty acids consist for the most part of oleic 30–35 per cent., linolic 40–45 per cent., and the balance mostly stearic. Holde, Selim and Bleyberg (*J.S.C.I.*, 1924, 43, B916) found 21·6 per cent. of solid acids and 78·3 per cent. of liquid acids.

Jamieson and Baughman have found that the free fatty acids of cotton-seed oil are in practically the same proportions as they occur as glycerides in the oils (*Cotton Oil Press*, 1923, F, No. 2, 35).

The colouring matter of cotton-seed is known as gossypol. It appears to have the empirical formula, $C_{13}H_{14}O_4$ or $C_{30}H_{28}O_9$. It is insoluble in water and dilute acids, but soluble in the usual organic solvents and in dilute alkalis. On account of the presence of about 0·6 per cent. of this compound the raw kernels are highly toxic (Carruth, *J.S.C.I.*, 1917, 36, 1285) but the cake is much less toxic on account of the transformations which take place. Thus the same worker (*J.S.C.I.*, 1918, 37, 319A) has separated four different gossypols which he differentiates as A, B, C and D and which have quite different degrees of toxicity, the D compound being the least toxic. The presence of gossypol may be detected by treating a portion of the meal with a drop of concentrated sulphuric acid and immediately examining the mixture under the microscope; if numerous red areas appear where the acid touches the more or less broken-up " glands," the presence of toxic unchanged gossypol is indicated. To determine the quantity of gossypol present, a quantity of the meal sufficient to yield about 10 grms. of oil is extracted with ether, the ethereal solution evaporated, and the residue of oil, after filtration, is mixed with about 10 per cent. of its weight of aniline; the mixture is warmed on a water-bath and then set aside. If, after several days, no precipitate is formed, the meal may be considered to be free from gossypol. In the presence of gossypol, however, a yellow crystalline precipitate separates; this is collected, washed first with a mixture of ether and petroleum spirit (1 : 2), then with petroleum spirit, dried at 100° and weighed. The compound appears to be the dianiline salt of gossypol ($C_{30}H_{28}O_9$, $2C_6H_5NH_2$) and its

weight is multiplied by 0·74 to obtain the quantity of gossypol. Cotton-seed meals containing 0·24 per cent. or more of gossypol proved fatal to rats within 10 days; meals containing smaller quantities were injurious to the animals.

Gossypol is present in glands in all but the woody tissues of the cotton plant. The very sparingly soluble aniline salt, of the average composition, $2C_{30}H_{30}O_9$, $5C_6H_5NH_2$, may be used for the separation and determination of gossypol. A more yellow substance, " B " gossypol, is formed by heating at 186°–190°, a white product, " C " gossypol, by fusion with alkalis, and another yellow compound, " D " gossypol, by cooking the cotton-seed for oil. All four substances give blood-red solutions in concentrated sulphuric acid and fine blue colourations when their alkaline solutions are exposed to the air. By suitably conducted cold pressing the oil cells of cotton seed may be emptied without the oil dissolving the contents of the resin glands, and no gossypol then enters the cotton-seed oil, but in the usual cold-pressing processes the seed is heated to a considerable extent and the glands ruptured, so that commercial " cold-pressed oil " contains about 1·5 per cent. of gossypol, that is about three-fourths of the whole. In the " hot-pressing " process, the gossypol is exposed to oxidising influences and changes largely into the less toxic " D " gossypol, most of which remains in the cake. Consequently, a " hot-pressed " oil should lose less on refining with alkali than a " cold-pressed " oil from the same seed (*J.S.C.I.*, 1918, 37, 319A).

Further work has been published by Schwartze and Alsberg (*J.S.C.I.*, 1924, 43, B22 and B885). They found in an examination of a number of different samples of cotton-seed that the quantity of gossypol varied directly with the percentage of oil, and found that the ether extract of cotton-seed kernels and pure gossypol derived in arachis oil were similarly toxic and that the toxicity of the extracts corresponded, with some variations, to the proportion of contained gossypol.

The unsaponifiable matter of cotton-seed oil has been investigated by a large number of workers. The total amount found has varied between 0·7 and 1·6 per cent. and appears to consist of sitosterol along with other bodies of an indefinite character. Bömer and Winter (*J.S.C.I.*, 1901, 20, 1147) found the M.Pt. of the sitosterol to be 136°–137° and that of the acetate to be 123·5°–124°, but state that a large number of crystallisations are necessary before the pure substance can be obtained.

Siegfeld (*J.S.C.I.*, 1904, 23, 742) found two substances, neither of which could be acetylated, having M.Pts. of 93° and 122° respectively, whilst he also isolated a sterol with M.Pt. 138·8°–139·8° the acetate of which had M.Pt. 131·5°–132·5°.

Matthes and Heintz (*Analyst*, 1909, 34, 362) resolved the unsaponifiable matter into a solid and a liquid portion. The solid portion consisted of a mixture of two substances, the first a sterol with M.Pt. 139°, and the second consists of a substance with M.Pt. 81°–82°. The liquid portion had B.Pt. 98°–300° *in vacuo*.

Waterman and Perquin (*J.S.C.I.*, 1924, 43, B525) have found that when the oil is decomposed at 450° in an autoclave in an atmosphere of hydrogen the oxygen is removed as oxides of carbon and water and that the remaining product is a hydrocarbon mixture containing a high percentage of petrol.

In various countries the oil has to be denatured for fiscal reasons when used for such purposes as soap manufacture. In France this may be done by adding to 100 kilos. of oil 100 grms. of nitrobenzene or 200 grms. of oil of rosemary (*J.S.C.I.*, 1911, 30, 498).

For some time it was considered that cotton-seed oil, along with other vegetable oils, was deficient in or devoid of the accessory food factors known

as vitamines, but Daniels and Loughlin have shown (*J.S.C.I.*, 1920, 39, 609A) that cotton-seed oil appears to contain notable proportions of fat-soluble A. That commercial cotton-seed oil is frequently deficient in this substance is apparently due to the treatment to which the oil is subjected during preparation.

The constituents of crude cotton-seed oil have been studied in a series of papers by Jamieson and Baughman. The *Cotton Oil Press* 6 (No. 4), 33; 7 (No. 2), 35; 7 (No. 5), 29. *J.O.F.I.*, 1924, 1, 30.

Anderson and Moore (*Analyst*, 1923, 48, 556) found that the unsaponifiable matter of cotton-seed oil contains at least two phytosterols, which may be separated by fractional crystallisation, one of these has M.Pt. 138° to 139°, $[\alpha]_D^{20} = -34{\cdot}19°$, and acetate of M.Pt. 124°, and the other M.Pt. 134° to 135°, $[\alpha]_D^{20} = -33{\cdot}61°$, and acetate of M.Pt. 119°.

TABLE XCI.—CHARACTERISTICS OF COTTON-SEED OIL

Authority.	S.G. 15°.	Sap. Value.	Iodine Value.	$n_D^{40°}$.	Sol. Pt. °C.	Titre. °C.	M.Pt. Acids. °C.	R.M.
Lewkowitsch	0·923–0·926	191–194·5	101–120·5	1·4643–1·4666	3–4	33·3–37·6	35–40	..
U.S.P.	0·915–0·921	190–198	105–114	..	0 to −5	..	..	..
Fryer & Weston	0·922–0·926	192–194	105–112	1·4646–1·4653	.. ..	33–37	.. ..	.. ..
Mitchell	0·913–0·930	191–196	104–116	...	0 to −1	..	..	0·7–0·9
Bolton & Revis	0·922–0·925	192–195	105–115	..	..	..	35–38	..
B.P.C.	0·918–0·925	..	102–108	1·4670–1·4679	0 to −5	32	36	..
Leach	0·922–0·925	193–195	108–110	1·4653–1·4665	3–4	32–35	35–38	1·0

TABLE XCII.—CHARACTERISTICS OF THE INSOLUBLE FATTY ACIDS

Authority.	Titre. °C.	M.Pt. °C.	Iodine Value.	Iodine Value of Liquid Acids.	M.M.W.
Lewkowitsch	33·3–37·6	35–40	105–115	141·9–151·7	275
Leach	32–35	35–38	111–115	..	..
B.P.C.	32	36	..	..	..
Fryer and Weston	33–37 *	..	..	147–151	..
Mitchell	..	34–40	111–116	142–152	..

* Natural oil; winter oil about 28°.

Some work showing how the characteristics of the oil are affected by heat treatment has been carried out by Fulmer and Manchester (*Analyst*, 1908, 33, 432), who obtained the results given in the following table:

TABLE XCIII.—EFFECT OF HEAT ON COTTON-SEED OIL (FULMER AND MANCHESTER)

	Specific Gravity at 15·5° C.		Refractive Index at 25° C.		Iodine Value. (Hanus.)		Saponification Value.		Free Fatty Acids.	
Normal unheated oil	0·9221		1·47509		110·1 per cent.		191·8		0·06 per cent.	
Temp.	Heated for		Heated for		Heated for		Heated for		Heated for	
°C.	10 min.	30 min.	10 min.	30 min.	10 min.	30 min	10 min.	30 min.	10 min.	30 mi
180	0·9227	0·9228	1·47510	1·47510	110·0	108·1	190·9	190·8	0·053	0·054
220	0·9229	0·9229	1·47518	1·47518	108·8	108·5	190·7	190·2	0·059	0·068
240	0·9229	0·9236	1·47528	1·47548	108·4	108·5	190·4	190·6	0·130	0·260
250	0·9236	0·9240	1·47535	1·47563	108·3	107·8	190·6	190·4	0·160	0·400
270	0·9234	0·9242	1·47549	1·47583	106·9	106·3	190·7	190·9	0·530	0·880

These results show that, in general, the specific gravity, refractive index and free acid increase whilst the iodine value decreases as the temperature and the time of heating increase. The changes, it will be noticed, are not very marked and an oil subjected to temperatures such as these will still yield figures within the normal limits of variation for the oil.

Arny, Kish and Newmark (*Analyst*, 1919, 44, 407) have developed a series of chemical colour standards for the classification of cotton-seed oils which may, of course, be used for other purposes. These standards, termed the Co-Fe-Cu standard are composed as follows: red, N/2 solution of cobalt chloride; yellow, a N/2 solution of ferric chloride; and blue, a N/2 solution of copper sulphate, all in 15 per cent. hydrochloric acid. With these solutions, blended in various proportions and diluted with various quantities of water the colour of any commercial samples of cotton-seed oil may be accurately matched. Experiments have shown that the Co-Fe-Cu standard solutions are perfectly stable and give identical results after keeping for four years; moreover they are readily controlled by analysis. The comparisons are conveniently made in 1 oz. round bottles with sufficient accuracy, and perfectly accurate results are obtained by comparison side by side in $\frac{1}{2}$ in. cells in the Lovibond instrument. The following limits for the specification of commercial grades of cotton-seed oil have been defined in terms of the above Co-Fe-Cu acid standards:

	From				To			
	Fe.	Co.	Cu.	Water to	Fe.	Co.	Cu.	Water to
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Prime white . . .	6	0·4	..	50	16·0	1·4	..	60
Choice summer yellow	22	3·4	..	50	33·3	3·3	..	50
Off summer yellow .	42	6·2	..	60	39·0	7·2	..	50

Properties.—Refined cotton-seed oil varies in colour from golden to nearly colourless—the crude oil obtained by hot expression may vary from brown to almost black. A certain amount of stearine separates out from the oil

at temperatures below 15° whilst at a temperature of about 0° it becomes almost solid. On account of the somewhat high melting-point of the oil a portion of the stearine is frequently removed by chilling and pressure (for characteristics of the separated stearine see below), in the case of oils intended to be used as salad oils with the production of the so-called " winter " oils; such oils will remain quite bright until cooled below the freezing-point of water and have a titre of about 28° and an iodine value of 110–116.

The New York Produce Exchange has laid down standards for the various qualities of oils. These standards, as quoted by Lewkowitsch, are as follows:

" Prime crude cotton-seed oil must be made from sound decorticated seed, must be free from water and foots, and must be sweet in flavour and odour. It should produce prime summer yellow oil when refined with caustic soda, with a loss in weight not exceeding 9 per cent. Should the loss in refining be greater than 9 per cent. but the oil obtained be still of prime summer yellow grade (and it cannot be rejected by the buyer), the price must be reduced by a corresponding amount.

" Choice crude oil must be manufactured from sound decorticated seed, must be free from water and foots, sweet in flavour, and odour, and should produce by proper methods of refining choice summer yellow oil, with no greater loss in weight than 6 per cent. for Texas oil and 7 per cent. from oil of other seeds. The percentage of free fatty acids should not exceed 1 per cent. (as oleic acid).

" Qualities which correspond to neither of the grades mentioned are termed ' off ' oil, and are sold by sample.

" Prime summer yellow oil is required to be clear, free from water and foots, sweet in flavour and odour, and of no deeper colour than 35 parts yellow and 7·1 parts red in Lovibond's tintometer. Choice summer yellow must be clear, free from moisture, and sweet in flavour and odour. Off summer yellow must be free from water and foots, and may be of lower quality as regards taste and colour. The refined oil is graded in the United States according to colour. The Interstate Cotton-Seed Crusher's Association has adopted as the standard for grading refined oil Lovibond's tintometer. Thus prime summer oil must not have a deeper colour at about 70° F. than is shown by the combination of 35 yellow units and 7·1 red units in Lovibond's tintometer."

" Prime winter white cotton-seed oil must be perfectly clear, straw-white to white in colour, sweet in flavour and dry, and must remain clear, at a temperature of 32° F. for five hours. Prime winter yellow cotton-seed oil must be transparent, free from water and foots, sweet in flavour and odour, straw-coloured (not reddish) and must remain clear at a temperature of 32° F. for five hours. The cold test relied upon must be carried out as follows: A 4 oz. sample bottle is filled with the oil, a thermometer inserted through the cork of the bottle and closed tight. The oil is then warmed slowly to 80° F. and allowed to remain at that temperature for fifteen minutes. It is then put into a box surrounded by ice and allowed to stand in the box for five hours. After this time it must still be clear, brilliant, and free from deposited stearine."

The oil is an excellent edible oil and is used in large quantities in the manufacture of margarine and lard substitutes and as a salad oil. The oil is one of the most important of those in the semi-drying class. The oxygen absorption in the modified Livache test is about 6·5 per cent. as compared with about 15 per cent. for linseed, and 1 per cent. for olive. The commercial oil is usually free from fatty acids on account of the alkali treatment

used during refining. Smith has stated (*Analyst*, 1920, 45, 370) that the Kreis reaction for rancidity is given by the crude oil and sometimes by the refined oil even when not rancid.

Colour Tests.—There are several colour tests which are more or less characteristic of cotton-seed oil. The most important is that of Halphen, whilst that with nitric acid is sometimes of value. Halphen's test is considered at length on page 79, whilst the less useful test of Becchi is described on page 80.

The nitric acid test is carried out by Lewkowitsch by well shaking about 5 c.c. of the oil with an equal volume of concentrated nitric acid (S.G. 1·375) * and the mixture then allowed to stand. Most seed oils give practically no reaction under these circumstances, but cotton-seed oil yields a brown colouration. The amount of colouration produced varies to a considerable extent with samples of oil from varying sources, but under the best conditions it may cause suspicion when as little as 10 per cent. of cotton-seed oil is present, but in other cases larger percentages than this might pass undetected by this test. The nitric acid test has one considerable advantage over the other colour tests for cotton-seed oil in that oils that have been heated to fairly high temperatures give the reaction almost as strongly as untreated oils. On the other hand, other oils beside-cotton seed have been known to give the reaction, thus rape oil gives in some cases a considerable darkening whilst Coste and Shelbourn (*J.S.C.I.*, 1903, 22, 778) found that some samples of Neat's-foot oil gave the reaction whilst, in some cases, the reaction is given by soya-bean oil. Generally speaking the test must be looked upon merely as a confirmatory test in those cases where the usual analytical constants have suggested the presence of cotton-seed oil. It has been found by Hiltner and Feldstein (*Analyst*, 1921, 46, 407) that the colour reactions of cotton-seed oil are also given by hollyhock-seed oil. Apart from the colour tests cotton-seed oil is characterised by a high solidification-point ("winter" oils will not have this) and high melting and solidification-points of the fatty acids. The chief diagnostic character is, however, the iodine value of the liquid fatty acids which is usually round about 145 or over. The following table due to Wallenstein and Finck (*J.S.C.I.*, 1895, 14, 78) gives some idea of the relationship of this figure in different oils:

TABLE XCIV.—IODINE VALUES OF VARIOUS OILS

OIL.	IODINE VALUE OF LIQUID F.A.
Cotton-seed	146·8–148·2
Niger-seed	147·5
Maize	140·7
Arachis	128·5
Rape	120·7
Lard, European . . .	95·2–96·8
,, American . . .	104·5
Tallow.	92·2–92·7

Official methods for the analysis of cotton-seed oil products have been fixed by the U.S. Interstate Cotton-Seed Crusher's Association. An abstract of these with modifications may be found in the *Journal of the Society of Chemical Industry* (*J.S.C.I.*, 1911, 30, 906; 1913, 32, 31 and 797; 1914, 33, 1060).

* Stronger acid gives less definite results.

Dickhart has suggested (*Analyst*, 1923, 48, 224) that it is possible to detect crude vegetable oils in crude cotton-seed oil by means of copper acetate. The test is carried out by shaking a petroleum spirit solution of the crude vegetable oils containing 10 grms. of the oil in 150 c.c. of solvent with 40 c.c. of a freshly prepared 5 per cent. aqueous solution of copper acetate; a green colour is produced in the oil solution in the case of the majority of oils. Crude cotton-seed oil does not show this reaction, and refined oils also give no colouration. Dickhart has applied this reaction to the detection of foreign oils in crude cotton-seed oil, a distinct colouration it is stated being produced by the presence of 0·5 per cent. of the adulterant.

This test, however, has been studied by Heller (*J.S.C.I.*, 1924, 43, B877), who says that Dickhart's statement that this reaction forms a good test for the presence of other raw vegetable oils in cotton-seed oil cannot be confirmed. The presence of 20 per cent. of raw unfiltered arachis oil in cotton-seed oil had no influence on the brown colour of the light petroleum layer.

It has been stated (*J.S.C.I.*, 1923, 42, 469A) that the oil is not suitable for adding to separated condensed milks on account of the fact that it cannot be made tasteless under these conditions.

Cotton-Seed Stearine.—Cotton-seed stearine is a by-product from the preparation of winter cotton-seed oils and is obtained in large quantities. The colour reactions and the composition of the acids are practically identical with cotton-seed oil itself although, of course, the proportion of solid acids is considerably higher in the former. The melting-point will depend to a considerable extent on the temperature and method of pressing but, as a rule, the bulk of the material is obtained under fairly similar conditions, so that average figures can be suggested as given in the table below:

Solidifying-point °C. . .	16–22
Melting-point °C. . . .	30–40
Saponification value . . .	194–195
Iodine value	89–95
Titre test °C.	35–42

Hydrogenated Cotton-Seed Oil.—A large amount of work has been done on the hydrogenation of cotton-seed oil, the hydrogenated product of which is widely used for various purposes. The Halphen test (q.v.) is largely affected,* the substance causing the colouration being gradually reduced in amount as the hydrogenation proceeds and finally destroyed altogether, although Kreis and Roth (*Analyst*, 1913, 38, 160) state that the product may be identified by means of Bellier's test which consists in heating the oil with nitric acid and a solution of resorcinol in benzene.

Bömer and Leschly-Hansen (*J.S.C.I.*, 1912, 31, 996) studied the effect of hydrogenation on various oils including cotton-seed oil. They found that a sample thus hydrogenated had M.Pt. 38·5°; Sol. Pt. 25·4°, $n_D^{40°}$, 1·4618; acid value 0·6; saponification value 195·7; iodine value 69·7; iodine value of liquid fatty acids, 115·6. They found that the Halphen reaction had been completely destroyed, but that the phytosterols had not been altered to any great extent. They state that Hauchecorne's reaction is still given by the hydrogenated product; this test is practically the nitric acid test described on page 222.

Mellana (*J.S.C.I.*, 1914, 33, 701) found in a sample of hydrogenated oil of M.Pt. 59°, that the titre was 50·3°, the saponification value 192·3 and the iodine value 41·0.

* Cf. Moore, Richton and Van Arsdel (*J.S.C.I.*, 1917, 36, 657).

The variation in the composition of cotton-seed oil during the process of hydrogenation has been studied by Myddleton and Barry, who find the figures given in the following table:

TABLE XCV.—EFFECT OF HYDROGENATION ON COTTON-SEED OIL (MYDDLETON AND BARRY)

	Original Oil.	After Hydrogenation.		
Iodine value	105·4	69·2	63·1	51·8
Palmitic acid	23·4	23·4	23·4	23·4
Stearic acid	..	6·5	9·6	18·6
Oleic acid	31·6	37·4	37·0	33·0
Linoleic acid	45·0	10·0	6·0	2·0
"Acids of hydrogenation"	..	22·7	24·0	23·0

Hilditch and Moore (*J.S.C.I.*, 1923, 42, 15T) have published a large amount of work showing the relative alteration in the characteristics produced by hydrogenation—this is well shown in the following tables taken from their paper:

TABLE XCVI.—EFFECT OF HYDROGENATION (HILDITCH AND MOORE)

Neutral cotton-seed oil and nickel on kieselguhr at 180°

Sample.	M.P. °C.	I.V. of Oil.	I.V. of Mixed Acids.	I.V. of Unsaturated Acids.	Per cent. of Unsaturated Acids.	Composition of Mixed Acids.		
						Per cent. Saturated.	Per cent. Oleic.	Per cent. Linoleic.
Original	liq.	109·1	114·1	151·6	75·3	24·7	23·8	51·5
No. 1	30	86·2	90·0	123·0	73·2	27	46	27
No. 2	35½	76·6	80·0	114·0	70·2	30	53	17
No. 3	39	65·9	68·8	95·4	70·0	30	66	4
No. 4	42	58·1	60·7	90·0	65·0	35	65	nil.
No. 5	46	49·1	51·3	90·0	57·0	43	57	nil.

Neutral cotton-seed oil and copper on kieselguhr at 180°

Sample.	M.P. °C.	I.V. of Oil.	I.V. of Mixed Acids.	I.V. of Unsaturated Acids.	Per cent. of Unsaturated Acids.	Composition of Mixed Acids.		
						Per cent. Saturated.	Per cent. Oleic.	Per cent. Linoleic.
Original	liq.	109·1	114·1	151·6	75·3	24·7	23·8	51·5
No. 1	liq.	100·8	105·2	139·8	75·0	25	34·5	40·5
No. 2	26	96·1	100·3	131·7	75·0	25	40·5	34·5
No. 3	35	77·4	80·3	108·0	74·3	25	60	15
No. 4	39	72·1	75·1	103·1	72·8	27	62	11
No. 5	40	65·2	68·0	94·3	72·1	28	68·5	3·5
No. 6	44	57·5	60·0	90·0	66·7	33	67	nil.

The following references may be consulted for further information.

" The Examination of Cotton and Cotton Wax." Piest, *Analyst*, 1912, 37, 202.

" Determination of Lint in Cotton-Seed Products by the Use of Zinc Chloride Solution." *Analyst*, 1915, 40, 403.

" The Causes and Prevention of the Heating of Cotton-Seed." *J.S.C.I.*, 1915, 34, 913.

" The Biochemical Changes in Cotton-Seed during Storage." *J.S.C.I.*, 1916, 35, 898.

" Comparison of the Digestibility of Palm-Kernel Cake, Extracted Palm-Kernel Meal, and Undecorticated Cotton-Seed Cake." Crowther and Woodman, *Analyst*, 1918, 43, 64.

" The Removal of Residual Fibres from Cotton-Seed and their Value for Non-Textile Purposes." De Segundo, *J.S.C.I.*, 1919, 38, 185A.

" The Determination of Husk in Cotton-Seed Cakes and Meals." Grimme, *Analyst*, 1914, 39, 173.

" A Method for the Determination of Crude Fibre in Cotton-Seed Meal." Francis, *Analyst*, 1915, 40, 443.

" The Determination of Nitrogen and Fat in Short Staple Cotton-Seed." Wells and Smith, *J.S.C.I.*, 1915, 34, 433.

" The Character and Suitability of Cotton-Seed as a Food Stuff." Osborne and Mendel, *J.S.C.I.*, 1917, 36, 562. Richardson and Green, *J.S.C.I.*, 1916, 35, 860; 1917, 36, 937, 1061.

" Methods of Approximating the Relative Toxicity of Cotton-Seed Products." Carruth, *J.S.C.I.*, 1917, 36, 1285.

" Phytic Acid in Cotton-Seed Meal and Wheat Bran." Rather, *Analyst*, 1913, 38, 419.

" Ethyl Ester of Linolic Tetrabromide as a Product in the Analysis of Cotton-Seed Oil." Palmer and Wright, *Analyst*, 1914, 39, 532.

" The Hydrogenation of Oleic Acid and Cotton-Seed Oil under Experimental Conditions." Shaw, *J.S.C.I.*, 1914, 33, 771.

" Methods and Catalysts for the Hydrogenation of Cotton-Seed Oil." Kahlanberg and Ritter, *J.S.C.I.*, 1921, 40, 268A.

CHAPTER XIV

Rape Oil (Colza Oil)

Commercial rape oil is obtained from the seeds of several varieties of *Brassica campestris*. There are a number of distinct botanical varieties, some of which are grown as winter seeds, but in the main the characteristics of the oils from the different varieties show a very close relationship, whilst in most countries, particularly in England, no distinction is made between them, although at one time the expression " colza oil " was undoubtedly confined to that expressed from the finest French seed and to that only. The seeds usually contain about 40 per cent. of oil.

The various varieties are cultivated to a wide extent in Europe (France, Germany and the South-East), India, China and Japan. The oil is obtained by crushing the seeds (which are proverbially small, an ounce sometimes including as many as 40,000 seeds) and then expressing the oil in presses or extracting with solvents. Edible oil is that expressed in the cold. The oil so obtained is usually somewhat dark coloured, that obtained by expression usually containing more mucilage than the extracted oil and to that extent being more impure. Refining, especially for burning oils, is carried out by treatment with about 1 per cent. of sulphuric acid (the strength used by various refiners varies from the concentrated acid to as low as 40 per cent. by volume) followed by thorough washing with water by decantation when a pale yellow oil, which should be free from mineral acid, is obtained. Oil refined by this process will contain a certain amount of free acid (formed by hydrolysis during the treatment) which renders the oil less suitable for lubricating purposes—for this reason the finest colza lubricating oil is refined by means of fuller's earth. Edible oil is frequently refined with caustic soda. The characteristics are practically unchanged by the process of refining with the exception of the fact already noticed that the free acid is slightly increased.

Composition.—The composition of rape oil has been the subject of numerous investigations. The oil is characterised by the fact that it contains large amounts of erucic acid which has such properties of its own that it can be isolated from a mixture of acids more readily than many of the other acids (*vide infra*). The saturated acids only occur to quite a small extent, probably not more than 1 per cent., of which at least a portion was found by Ponzio (*J.S.C.I.*, 1894, 13, 257) to be identical with the mixture of arachidic and lignoceric acids obtained from arachis oil. Archbutt (*J.S.C.I.*, 1898, 17, 1009) found various samples of oil to give quantities of " arachidic acid " varying from 0·3 to 1·4 per cent., the melting-point in the last case being as high as 73°.

Holde and Wilke (*J.S.C.I.*, 1922, 41, 598A) subjected the oil to the process of alcoholysis, and by this means and subsequent purification produced a pure erucic acid.

Raymond (*J.S.C.I.*, 1922, 41, 508A) was able to identify the following acids, namely, erucic, linolic or linolenic, palmitic, oleic and stearic, whilst Toyama (*J.S.C.I.*, 1922, 41, 988A) found that the erucic acid content was about 65 per cent., the content of saturated acids being less than 2 per cent., and stated that the other acids isolated or strongly suspected were stearic,

behenic, lignoceric and arachidic, oleic, linolic and linolenic. For hardened rape oil see Normann and Hugel (*J.S.C.I.*, 1917, 36, 658).

The sterol of rape oil consists of a mixture of substances which have not yet been definitely separated. According to Windaus and Welsch, brassicasterol occurs having M.Pt. 148° (acetate 157°–158°), whilst another sterol is present having M.Pt. 142° (M.Pt. of acetate 134°). Steuart found that the acetate had a M.Pt. varying from 139°–129° and gives no indication of any substances having a higher M.Pt. although his sample contained paraffin which may have interfered with the separation.

TABLE XCVII.—CHARACTERISTICS OF RAPE OIL

Authority.	S.G. 15°.	Sol. Pt. °C.	Sap. Value.	Iodine* Value.	n_D^{40}.	R.M.	Unsap. Per cent.	Acid Value.
Lewkowitsch . .	..	−10	171·7–176·5	93·5–103·6	1·4630 1·4670	..	0·5–1·0	..
Mitchell . . .	0·914–0·916	−10	170–175	97–105	..	0·0–0·7	..	..
Bolton and Revis	0·913–0·917	..	168–178	94–104	..	..	0·8–1·7	Usually below 2·0
Fryer and Weston	0·914 0·917	..	170–177	97–105	1·4652–1·4659	..	0·5–1·0	Not exceeding 4·0
Grimme . . .	0·917–0·923	−4 to −12	171·3 180·3	93·6–104·6	1·4637–1·4666	..	0·7–1·4	..
Crossley and Le Sueur	0·914–0·918	..	167·7–174·1	94·1–104·8	1·4652	0·0–0·8	..	1·4–4·0

TABLE XCVIII.—CHARACTERISTICS OF THE FATTY ACIDS

Authority.	M.Pt. °C.	Titre. °C.	Iodine Value.	Iodine Value of Liquid.
Lewkowitsch	18–22	11·7–13·6	99·8–105·6	120–126
Mitchell	16–21	..	..	..
Fryer and Weston . .	..	12–13	..	..
Bolton and Revis . . .	19–21	..	..	..
Grimme	11–21	6–19	98·0–107·1	..

* It is unusual for the iodine value of genuine East India rape oil to exceed 101.

Properties and Special Tests.—Rape oil is light yellow to deep brown in colour, depending upon the method of preparation and the extent of refinement. It has a characteristic odour and flavour which are only pleasant in the very finest oils. The oil is fluid at ordinary temperatures; a quantity of stearine is usually present at room temperature or below but the oil does not completely solidify until below freezing-point. The most characteristic property of rape oil is its high viscosity, which is the highest of any oil except castor; the identification of the oil depends upon this factor together with the low saponification value and the presence of erucic acid. The Livache test gives an absorption of about 2·5 compared with about 15 for linseed oil.

There are no specific colour tests for the oil which are of serious value, although Milrath has suggested a test for the detection of whale oil (*Analyst*, 1907, 32, 427) which depends upon the brown colour developed by heating such a mixture with syrupy phosphoric acid. The low saponification value is of the greatest value in the examination of rape oil itself and for its detection in mixtures with other oils. The high viscosity (see viscosity, page 102) is also a valuable test, particularly in those cases where the oil is intended as a lubricant.

The main chemical tests for rape oil are those which depend upon the characteristic properties of erucic acid. This acid, although unsaturated, forms a lead salt which is practically insoluble in ether and so differs from the lead salts of the other insoluble acids, all of which (with the exception of the oleic acid which is produced during the process of hydrogenation) are freely soluble in this solvent. The method of separating erucic acid depends therefore, in the first place, upon the separation of the liquid and solid fatty acids and subsequently the determination of the iodine value of the solid acids which will include erucic acid. This is the better method of working, although Holde and Marcusson (*Analyst*, 1910, 35, 401) base a method of separation upon the solubility of this acid in 96 per cent. alcohol at −20° and its insolubility in 75 per cent. alcohol at the same temperature.

The method of working usually adopted is that suggested by Tortelli and Fortini (*Analyst*, 1910, 35, 401), who depend not only upon the iodine value of the solid acids, but also upon the critical temperature of solution of the alcoholic solution of the sodium salts of the liquid fatty acids. This method has been examined by Fryer and Weston (*Technical Handbook of Oils, Fats and Waxes*, Vol. II, page 135) and is here described in the form recommended by them:

Into the 200-c.c. flask weigh 20 grms. of the oil, add 50 c.c. of 2N alcoholic potash, made up as follows: Dissolve 56·0 grms. of KOH (" pure from alcohol ") in 45 c.c. water; make up to 500 c.c. with absolute alcohol, or dissolve the potash in its own weight of water, and make up to 500 c.c. with purified " industrial " methylated spirit (non-mineralised) about 91 per cent. strength, and saponify under a reflux condenser. Add a few drops of phenolphthalein solution and neutralise by titrating with 10 per cent. acetic acid. Into a 500 c.c. wide-necked conical flask place 20 grms. lead acetate, and dissolve in 300 c.c. of boiling distilled water. Slowly pour the neutralised soap solution into the boiling acetate, shaking constantly as the lead salts separate. Cool under the tap, rotating the flask meanwhile to cause the salts to adhere to its sides. Pour off the aqueous liquor into a large beaker, returning any particles of lead salts that run off to the flask. Wash the lead salts with 200 c.c. of warm water (70°) three times, finally draining flask, and removing any adherent moisture from the lead salts by means of a wad of dry cotton-wool. Add to the flask 80 c.c. of ether, cork securely and well shake till the salts are broken up. Place under reflux condenser and heat

by applications of hot water to flask, shaking at intervals, for 15 minutes. Cork flask, and place in water at 15° for 1 hour, then pour contents on to a filter in a funnel placed in the mouth of a 500 c.c. separator and cover with watch glass till the ethereal solution has filtered through. The filter-paper with the insoluble lead salts is transferred to the flask again, boiled and cooled as before with a further 40 c.c. of ether, and filtered through a fresh paper. After draining, any remaining lead salt in the flask is washed out on to filter with a further 40 c.c. of ether, and this is allowed to drain through. The filter-paper containing the insoluble lead salts is placed in a beaker, a little pumice powder added, and boiled for half an hour with 50 c.c. of 20 per cent. hydrochloric acid solution, making up for any loss, by evaporation, of acid. The liquid is run into a separating funnel, cooled to 15°, 50 c.c. of ether is then added, the separator shaken and allowed to stand. The aqueous liquor and precipitated lead chloride are then run off, the ether layer shaken with 20 c.c. of 10 per cent. HCl, allowed to stand, the acid removed, and the ether washed with three successive quantities of 20 c.c. of water. The ethereal solution is run into a small flask, the solvent evaporated off, and the acids dried at 100° in the water-oven. The M.Pt. of the fatty acids and the iodine value are then determined. Tortelli and Fortini obtained the following results:

TABLE XCIX.—RESULTS OF CHEMICAL TESTS (TORTELLI AND FORTINI)

	Iodine Value of Solid Fatty Acids.	Melting Point of Solid Fatty Acids.	Critical Temperature of Solution of Sodium Salts of Liquid Fatty Acids.
		°C.	°C.
Olive oil	7·8	58–59	24–20
Rape oil	62·0	41–42	50–45
Olive oil 50% rape oil .	32·0	47–48	40–35
„ 30% „	28·0	48–49	35–30
„ 20% „	22·1	50–51	35–30
„ 10% „	12·8	54–55	34–30
Sesamé oil	9·3	55–56	20–18
Arachis oil	13·0	57–58	22–18
Cotton-seed oil . . .	19·0	57–58	16–14

Kreis and Roth (*Analyst*, 1913, 38, 114) base the detection of rape oil in other oils on a method depending upon fractional precipitation of the lead salt. The work has been extended by Kreis who, in a later paper (*Analyst*, 1913, 38, 434), states that 5 per cent. of rape oil may be detected in olive oil by means of the following process: The fatty acids from 20 grms. of the oil are dissolved in 100 c.c. of 95 per cent. alcohol and the boiling solution is treated with 1·5 grm. of lead acetate dissolved in 50 c.c. of alcohol. After standing for twelve hours at a temperature below 15°, the lead salts are collected, washed three times with alcohol, and the fatty acids are liberated from the salts by treatment with hydrochloric acid. The fatty acids thus obtained are again dissolved in 100 c.c. of alcohol, and the boiling solution is treated with 1 grm. of lead acetate dissolved in 50 c.c. of alcohol. After twelve hours the lead salts are separated by filtration, and the fatty acids remaining in the filtrate are recovered by evaporating off the alcohol and

treating the residue with dilute hydrochloric acid. The melting-point of this fraction of the fatty acids is now determined. In the case of pure olive oil it will be about 47°, but is considerably lower when rape oil is present.

Biazzo and Vigdorcik (*Analyst*, 1917, 42, 86) use a somewhat lengthy process which depends upon the potassium-salt-acetone method of separating fatty acids, followed by precipitation of the lead salts, hydrogenation of the acids so obtained and the further separation of the hydrogenated acids by means of their lead salts. This method would appear to be too lengthy for general use and to offer no particular advantage over that of Tortelli and Fortini.

Thomas and Yu (*Analyst*, 1923, 48, 128) have proposed another method for the separation of solid and liquid acids depending upon the solubility of their magnesium soaps in 90 per cent. alcohol. They have applied this method to the detection of rape oil in mixtures, when they were able to isolate fairly pure specimens of erucic acid from samples of rape oil. This method would appear to have possibilities and should be examined at length.

Adulteration.—The most common method of adulteration of rape oil is the addition of mineral oil. Such mixtures are frequently sold as " burning colza " but a large number of samples submitted simply as colza oil are grossly adulterated. During one period, out of fifty samples examined by the writer sixteen samples contained proportions of light mineral oil varying from 80 to 7 per cent. This adulteration will be shown by an increase in the unsaponifiable matter which is not more than 1·5 in a genuine oil and usually also by the change in the specific gravity, iodine value and refractive index. The amount of light mineral oil may be determined by heating 2 grms. in a flat bottom metal dish on the water-bath until no further loss occurs—a genuine oil usually gains about 0·6 per cent. under these conditions and a suitable correction may be made if necessary.

Rosin oil is also a likely adulterant either with or without mineral oil. It may be detected by the Liebermann Storch test, from the increase in the unsaponifiable matter, and from the alteration in the specific gravity and refractive index, although light mineral oil and rosin oil will tend to neutralise one another in the two latter characteristics.

Other seed oils, e.g. German sesamé, are sometimes used as adulterants when the price of these is low and that of rape oil is high. This will be detected as a rule by a reduction in the viscosity and an increase in the saponification value. Linseed oil would be detected by the insoluble bromide value (about 2–3 in the case of rape oil) whilst cotton-seed oil might be detected by the Halphen reaction. The titre test may frequently be of advantage as that of rape oil, 12° to 13°, is particularly low.

Other oils of the *Cruciferæ* are sometimes used as adulterants. Where only small quantities are added it is almost impossible to detect them, but where this type of adulteration is practised complete substitution usually takes place; such substitution may usually be detected with more or less certainty by a consideration of the usual characteristics together with the smell and taste. The constants of some of these oils are given below under ravison oil, jamba oil and charlock-seed oil.

The two following miscellaneous references may be noted.

L. Bussard, " The Greening of Colza Seed Cake." *J.S.C.I.*, 1911, 30, 643.

W. B. Smith, " Index of Refraction of the Mixed Fatty Acids of Rape Oil," *J.S.C.I.*, 1912, 31, 139.

Ravison oil.—Ravison oil is obtained from a variety of *Brassica campestris*, the Black Sea rape seed. The oil itself is similar to rape oil, but, as usually marketed, it is not suitable for use as an edible oil, whilst its higher iodine value and better drying properties render it much less suitable as a lubricating oil. The following are typical characteristics for the oil, the iodine value and decreased viscosity (about 10 per cent. less than rape oil) being valuable diagnostic features:

Specific gravity at 15·5°	0·918–0·921
Saponification value	173–178
Iodine value	110–120
Iodine value of insoluble acids	126
Iodine value of liquid acids	124

Jamba Oil.—Jamba oil is obtained from a somewhat ill-defined variety of *Brassica* which is closely related to rape seed. The oil is, however, inferior to true rape oil as it is not possible to produce from it a "blown oil" of satisfactory quality. The taste and smell render the oil fairly easy to detect. Typical characteristics are given in the following table:

Specific gravity at 15·5°	0·915
Saponification value	172–175
Iodine value	95–104
Titre °C	11–16
M.Pt. of acids °C.	19–21
Iodine value of acids	96

Charlock-Seed Oil.—This oil (obtained from *Brassica arvenis*) has been examined by Bailey and Burnett, who obtained the following results:

TABLE C.—RESULTS FROM CHARLOCK-SEED OIL (BAILEY AND BURNETT)*

	Expressed Oil.	Oil Extracted by	
		Ether.	Petroleum Spirit.
Sp. gr. at 15°/15°	0·9221	0·9272	0·9212
Refrac. index at 40°	1·4670	1·4685	1·4674
Saponif. value	182·9	183·1	181·0
Iodine value (Hanus)	121·1	119·8	119·3
Insol. acids and unsap. matter	95·3	95·4	95·2
Soluble acids	0	0	0
Mean mol. wt. of insol. acids	339·1	338·1	334·8
Percentage of liquid acids	89·3	90·0	90·0
Iodine value of liquid acids	126·0	122·3	125·0
Percentage of solid acids	3·1	1·6	2·0
Iodine value of solid acids	..	62·0	61·0

* *J.S.C.I.*, 1916, **35**, 696.

CHAPTER XV

Sesamé Oil

Sesamé oil is obtained from the seeds of the sesamé plant, *sesamum indicum*, of which several varieties or sub-species are known. Commercially the seeds are known as white or black. According to the rules of the trade, the white sesamé must contain at least 85 per cent. of white seeds. If the proportion of dark seeds exceeds 15 per cent., an allowance is made, when the proportion of dark seeds exceeds 25 per cent., the term white sesamé no longer applies (Lewkowitsch). The plant is probably a native of Southern Asia but it is now cultivated in many tropical countries, particularly in India and the Far East and in those countries bordering on the eastern and south-eastern portion of the Mediterranean.

The seeds contain a large proportion of oil, the published figures varying from 47 to 60 per cent., the average figure being from 50 to 55 per cent. Ether usually extracts from the seeds about 2 per cent. more oil than does petroleum spirit. The expression is usually carried out in three stages. The first expression, carried out in the cold, yields the finest oil particularly suitable for edible purposes, the second and third expressions are carried out at a higher temperature and yield inferior but still good oils. Unsound seed is now frequently extracted and the extracted meal used as a fertiliser, but the extraction process is making headway and it is quite likely that in the case of sesamé oil, as with other oils, the bulk of the oil of the future will be obtained by extraction.

There is a food-stuff which was used in Turkey and known as Tachîm. It was composed of the sesamé seeds ground up with the contained oil. It was occasionally ground up with sugar to make a kind of nougat and was suggested in the early part of the war as a possible ration.

The cold-drawn oils are usually of sufficiently good flavour for use without further refinement beyond settling and filtration. The lower qualities are refined by treatment with an aqueous solution of caustic soda (sometimes followed by treatment with a small quantity of dilute hydrochloric acid) removal of the precipitated colouring matters and impurities by decantation and treatment with fuller's earth.

Composition.—Sesamé oil contains (Lane, *J.S.C.I.*, 1901, 20, 1083) 12 per cent. to 15 per cent. of solid fatty acids and 75 to 80 per cent. of liquid fatty acids, the latter of which consist for the most part of oleic and linolic acids.

Jamieson and Baughman (*Analyst*, 1924, 49, 236) have examined the oil at some length and find that the oil contains *glycerides* as follows: Oleic, 48·1; linolic, 36·8; palmitic, 7·7; stearic, 4·6; arachidic, 4·0; lignoceric, a trace. Their sample of oil contained 1·7 per cent. of unsaponifiable matter.

The unsaponifiable matter, which usually amounts to a little over 1 per cent. (Lewkowitsch gives as the limits 0·95–1·32), has been studied by a number of workers who find that several substances are present.* The phytosterol has a melting-point of 137°–139°, whilst that of the acetate is

* Cf. Schaefer, *J.S.C.I.*, 1919, 38, 505A. Steuart gives 1·52 per cent.

about 129°–130°, although a figure as low as 122° has been found by Steuart. In addition to the presence of sterol other substances are present, one of which, sesamin, is strongly dextrorotatory, and also a thick non-crystallisable oil which gives the Baudouin test mentioned below. This subject cannot yet be considered as in any way settled and further work along these lines is desirable.

Marcusson and Meyerheim (*J.S.C.I.*, 1916, 35, 549) make use of the optical rotation of sesamol (which they give as $[\alpha]_D = 52°$) for the detection of sesamé oil in other oils.

For further information reference may be made to the following papers: Merkling, *J.S.C.I.*, 1888, 7, 45. Tocher, *P.J.*, 1891, 639; 1893, 50, 700. Villavecchia and Fabris, *J.S.C.I.*, 1894, 13, 69. Malagnini and Armanni, *Analyst*, 1907, 32, 391.

TABLE CI.—CHARACTERISTICS OF SESAMÉ OIL AND FATTY ACIDS

Authority.	S.G. 15°.	Sap. Value.	Iodine Value.	n_D^{40}.	Sol. Pt. °C.	R.M.	Acid Value.
Lewkowitsch .	0·920–0·926	188–193	103–115	1·4655–1·4671	−4 to −6	..	..
Mitchell . .	0·921–0·924	188–193	102–117	..	..	1–2	..
U.S.P. . .	0·920–0·925	188–193	103–112	..	..	..	..
B.P. . . .	0·921–0·924	189–193	103–114	1·4650–1·4675	..	..	not more than 8
Fryer and Weston . .	0·921–0·925	188–193	103–110	1·4657–1·4659	..	..	about 5
Revis and Bolton . .	0·922 0·924	188–193	103–110	1·4652–1·4662	..	..	..

CHARACTERISTICS OF THE MIXED FATTY ACIDS

Authority.	Sol. Pt.	M.Pt.	I.V.	I.V. Liquid Acids.	Neutralisation Value.
Lewkowitsch . . .	21–24	24–30	109–112	1400–13	196–201

Properties and Special Tests.—Sesamé oil, also known as teel oil and gingili oil, is pale-yellow in colour, practically without odour, and having a slight agreeable taste. It is usually classed among the semi-drying oils

but actually its drying powers are not very much greater than those of olive oil and are considerably less than those of cotton-seed oil. The most noteworthy characteristic of the oil is its optical activity, all oils giving a definite positive rotation which varies from 0·8° to 2·4° in a 200 mm. tube, although figures as high as 9·0° have been recorded; this latter figure must, however, be looked upon as suspiciously abnormal. Castor, croton and rosin oils are the other optically active oils which are likely to be met with under ordinary conditions (cf. chaulmoogra oil, etc.); in the absence of these oils the optical activity of sesamé oil may be of some assistance in its identification.

Sesamé oil gives several characteristic colour reactions of which the most important, the Baudouin test, with its modifications and shortcomings are dealt with on page 82. Many of the others are of minor importance but a few are selected for special mention on account of their utility in special circumstances. The colour producing substances tend to pass into the milk of animals feeding on the oil, thus Engel (*Analyst*, 1906, 31, 158) examined the milk obtained from three wet-nurses after giving them fairly large doses (100 grms. at a time) of sesamé oil. He found that the fat always gave the Baudouin reaction after an interval of only one and a half hours between the feeding and taking the sample, a longer time being needed before the iodine value increased. He also found that when the sesamé oil was taken only once, or only for a few days, the fat gave the reaction for the whole period of time during which the iodine number reached its maximum, and that then an interval occurred during which no reaction could be obtained, followed by a third period, on the same day as the second, during which the reaction again occurred. If, however, sesamé oil is administered over longer periods, these three intervals lose their distinctness, and the reaction is obtained even after the iodine value has begun to decrease.

Soltsien's test is especially useful in testing margarines for sesamé oil in those cases where colouring matters have been added (which give a reaction with Baudouin's reagent and which cannot readily be removed by washing with hydrochloric acid), since these are reduced and rendered colourless. The test may be carried out by mixing the oil with an equal volume of stannous chloride solution and heating in the boiling water-bath when a red colouration is produced. It has been found, however, that the delicacy of the reaction is impaired if the constituents of the mixture remain too long in intimate contact so that to obviate this difficulty the following modification has been used: 5 c.c. of the oil are dissolved in 10 c.c. of petroleum ether and 2·5 c.c. of concentrated stannous chloride solution (prepared by mixing 5 parts of crystalline stannous chloride with 1 part by weight of hydrochloric acid, completely saturating with hydrochloric acid, gas, decanting and, if necessary, filtering through asbestos) are added. The mixture is thoroughly shaken, until a homogeneous mixture results, but not longer, and immersed in water at 40°. After the stannous chloride solution has separated out, the test-tube is placed in water at 80° in such a manner that only the stannous chloride solution becomes warm and the petroleum ether layer does not commence to boil. In the presence of sesamé oil the stannous chloride solution is stated to show after warming for 3 minutes a distinct red colouration.

Soltsien (*Analyst*, 1906, 31, 266) is of opinion that the furfurol reaction and the tin reaction of sesamé oil are not due to one and the same substance. Both the compounds can be extracted by shaking the oil with alcohol of 90 per cent. strength, but thorough extraction with hydrochloric acid of specific gravity 1·125 removes the substance that gives the furfurol reaction,

whilst the oil still gives the tin reaction as strongly as before. This opinion is also held by Zimmermann (*J.S.C.I.*, 1912, 31, 443), who states that 1 per cent. of sesamé oil will give the Soltsien reaction. (Cf. Utz, *J.S.C.I.*, 1913, 32, 950.)

Lewkowitsch, who does not recommend this test, states that the reaction is no longer given by rancid sesamé oil and that fat extracted from cakes and pastry prepared with pure butter always gives a red colouration.

Tocher tests for the oil by shaking 15 c.c. of the oil for about 30 seconds with a freshly made practically colourless solution of 1 grm. of pyrogallol in 15 c.c. of concentrated hydrochloric acid (S.G. 1·16). The aqueous portion is filtered through a wet filter-paper and heated for 15 minutes on the boiling water-bath. Sesamé oil gives a reddish-purple fluorescent solution. According to Bellier this reaction is not given by certain genuine olive oils which give a positive reaction in the Baudouin test, but this may quite easily be due to the greater delicacy of the latter reaction.

Guarneri's test for sesamé oil (*Analyst*, 1912, 37, 62) consists in treating the sample with a few drops of an ethereal solution of hydrogen peroxide and a little nitric acid of sp. gr. 1·4, when a blue colouration should be obtained in the presence of sesamé oil. A similar test has been described by Kreis. Utz (*Analyst*, 1912, 37, 62) described a series of systematic tests made upon different oils and fats, from which he concludes that the colours obtained in the case of mixtures are not sufficiently distinctive, and that the reaction is not sufficiently sensitive. The Baudouin test and Soltsien's tin chloride reaction are much more reliable and sensitive than Guarneri's reaction. (Cf. Bosch, *J.S.C.I.*, 1915, 34, 288.)

Bellier's test consists in shaking 2 c.c. of the oil with 2 c.c. of a saturated solution of resorcinol in benzene and 2 c.c. of concentrated nitric acid. Steiner (*J.S.C.I.*, 1923, 42, 676A) considers that this test is useless in general for the detection of the admixture of vegetable fats with butter. The sensitiveness of the reaction is far less in the case of butter than in that of lard. As a special test for sesamé oil, however, it is at least equal in sensitiveness to Baudouin's reaction, and is useful for confirming an uncertain Baudouin reaction.

Adulteration of sesamé oil is not unknown. Of the oils used as substitutes or adulterants the more common are rape, poppy-seed, cotton-seed or arachis. For the purposes of detecting adulteration the iodine value (poppy-seed oil) titre (cotton-seed oil) and saponification value (rape oil) are most likely to be of value, whilst arachis oil may be detected and determined by the usual methods. The adulteration of other oils with sesamé is not frequently practised on account of the ease with which an average sample of sesamé oil can be detected by means of the colour tests.

Hydrogenated sesamé oil has been studied by Paul and Roth, who found that when the iodine value was reduced to about 2·0 the M.Pt. was about 69°. They found that with increasing reduction the intensity of the Baudouin reaction became less and less and when the iodine value became as low as 2·0 became very faint. When the hydrogenated fat was allowed to stand the intensity of the Baudouin reaction increased, but did not again become equal to that of the original oil.

An oil, obtained from the seeds of *Ceratotheca sesamoides*, has been described by Bolton (*Analyst*, 1919, 44, 233). The seeds from which the oil is obtained closely resemble those of the sesamé plant and the oil itself has very similar characteristics. Thus Bolton found:

Specific gravity 15·5 . .	0·916
n_D^{40}	1·4656
Saponification value . .	190·2
Acid value	1·2
Iodine value	110·6

This oil may be distinguished from sesamé oil in that it does not give the Baudouin reaction, neither does it give the Halphen reaction for cotton-seed oil.

German sesamé oil (dodder oil, cameline oil) is obtained from the seeds of *Camelina sativa*, Crantz, a plant which was at one time largely grown in Germany. The seeds contain some 30–35 per cent. of a light yellow oil having a peculiar pungent odour, of which about 28 per cent. may be obtained by expression in the hot and about 28 per cent. by extraction with solvents. The oil, which probably contains the glycerides of oleic, linolic, palmitic and erucic acids, has only slight drying properties and is chiefly used as a substitute for or an adulterant of rape oil, the iodine value of which it will increase. The following characteristics have been observed:

TABLE CII.—CHARACTERISTICS OF GERMAN SESAMÉ OIL

Observer.	S.G. 15°.	Sol. Pt. °C.	Acid Val.	Sap. Value.	Iodine Value.	n_D^{40}.	Unsap %.	Titre. °C.
De Negri and Fabris . . .	0·926	..	..	188	135·3	..	..	13–14
Grimme * . .	0·922	−15 to −16	13·2	185·5	135·1	1·4688	1·16	15–16
Other observers .	0·924–0·926	−18	..	..	142·4	..	..	..

* *J.S.C.I.*, 1912, 31, 500.

CHAPTER XVI

NON-DRYING OILS

Calumpang Nut Oil

This oil, also known as Java olive oil and sterculia oil, is obtained from the seeds of *Sterculia fœtida*, L. The seeds which are known as Java olives or Beligno seeds, are described by Wedemeyer (*Analyst*, 1906, 31, 361) as follows: "The Java olive is the seed of one of the *Sterculiaceæ*, and consists of an outer parchment-like husk enclosing a hard shell, which contains the fleshy part of the seed. The shell yields about 10 per cent. of a yellow, butter-like fat, and the fleshy part 46·6 per cent. of a bright yellow oil, whilst the whole seed (husk, shell and flesh) yields 30·3 per cent. of oil. This oil from the whole seeds is similar in appearance to olive oil, has a slightly rancid smell, but an agreeable taste."

Oil is contained both in the skin and pulp (to the extent of about 10 per cent.) and in the kernels (which contain up to 50 per cent. of oil) the whole seeds yielding about 30 per cent. on extraction; higher figures have been obtained by other workers, but there is some confusion between the oil in the kernels and in the whole seeds. The oil gives a well-marked Halphen reaction.

Table CIII.—Examination of Calumpang-Nut Oil

Authority.	Source of Oil.	S.G. 15°.	Sap. Value.	I.V.	n^{40}.	Titre.	Acid Val.	Sol. Pt.	R.M. Value.
Wedemeyer	Whole seed	·926	187·9	76·6	1·4654	..	..	..	0·8
Bontoux .	Pulp oil	..	172·4	81·4	..	..	Expressed oil.		
,, .	,,	..	192·8	58·7	..	..	Extracted with petroleum ether.		
,, .	,,	..	193·8	56·3	..	43	Extracted with carbon bisulphide.		
,, .	kernel oil	..	173·4	81·4	..	..	Extracted with petroleum ether.		
Hooper .	,,	[4] ·919	199·3	83·0	..	31·5	..	..	..
[3] Bolton and Jesson .	Pulp oil	..	..	66·3	1·4680	..	..	..	..
,,	Kernel oil	..	193·8	75·8	1·4658	..	1·0[5]	−6	..
Brill and Accaoli [6]	Kernel oil	·925	212·2	76·1	1·4645	..	0·3	..	..
[1] Georgi .	Pulp oil	[2]0·8561	191·2	69·7	1·4578	30–31	74·2[5]	..	..
,,	Kernel oil	0·8676	180·2	62·3	1·4620	50·3	10·6[5]	..	..

[1] *J.S.C.I.*, 1923, 42, 462A. [2] At 100/15·5. The seeds were mouldy when examined. Unsaponifiable matter was 3·7 and 5·6 per cent. respectively. [4] At. 30·5. [3] The seeds are described by these authors as Kalœmpang beans or Beligho seeds. *Analyst*, 1915, 40, 3. [5] Oleic acid per cent. [6] *Ibid.*, p. 505.

Bontoux (Lewkowitsch, *Technologie et Analyse chimiques des huiles, graisses et cires*, traduit par E. Bontoux, Vol. II, p. 902) has examined separately the oils obtained from the pulp and kernels of seeds furnishing 17 per cent. of skin and pulp, 30 per cent. of husks and 53 per cent. of kernels. The skin and pulp yielded by extraction with carbon bisulphide 28·6 per cent. and the kernels 53·6 per cent. of oil respectively. The fatty matter obtained from the former was a light yellow pasty mass, becoming clear on warming above 30°. The expressed fat has a pleasant odour and taste.

The kernel oil differs from the pulp oil in its behaviour on heating to 240°–245° (Wedemeyer) when it is suddenly converted, with considerable generation of heat, into a solid india-rubber-like substance; the substance obtained is insoluble in the usual solvents. This property has doubtless something in common with the high figure 163, given by this oil in the Maumené test which, taken into consideration with the iodine value, is characteristic of this oil. The composition of the oil has not yet been determined.

It is somewhat difficult if not impossible to reconcile the data given by various workers. Some of the variations recorded are doubtless due to the decomposition of the oil as in the case of the seeds examined by Georgi, which were mouldy, but even a theory of this kind will not explain such diverse figures for the saponification value as 212 and 173. Further work is desirable.

Oil from *Canarium* Species

Many species of *Canarium* such as *C. Commune*, *C. Oleosum*, *C. polyphyllum*, yield edible fruits somewhat resembling almonds, the kernels of which yield considerable quantities of oil.

The following results have been recorded:

Table CIV.—Examination of Oils from *Canarium* Species

Observer.	Species.	Acid Value.	Sap. Value.	Iodine Value.	n^{40}.	Titre. °C.	M.Pt. °C.	R.M.	Per cent. Oil in Kernel.	Uns pe cen
Wedemeyer	*Commune*	22·8	193·5	64·7	1·4590	37·2	..	0·1	72	..
Pastrovich .	,,	1·3	194·3	65·6	1·4601	41·0	28·5	0·0	66	0·4
Grimme .	*Oleosum*	..	197·0	63·0	1·4591	..	..	..	..	0·9
Krause .	*Polyphyllum*	..	200·2	59·7	1·4679	..	30	4·41	68	..
Wagner and Lampart .	,,	..	189·7	53·0	..	..	..	0·3	..	..

Several species of *Canarium* have been examined at the Imperial Institute (*Analyst*, 1915, 40, 239) with results as given in the following table:

Species.	Moisture per cent.	Crude Proteins per cent.	True Proteins per cent.	Fat per cent.	Starch, etc., per cent.	Fibre per cent.	Ash per cent.	Nutrient Ratio.*	Foo Unit
C. commune ‡	2·9	13·5	12·9	72·3	7·4	trace	3·9	1 : 12·3	221
C. rufum ‡ .	3·9	16·4	15·5	70·5	4·2	trace	5·0	1 : 10·1	231
C. colophania	4·2	15·9	15·3	64·6	9·0	2·1	4·2	1 : 10·0	210

* The ratio between the percentage of crude proteins and the sum of the percentages of starch and fat, the latter being first converted into its starch equivalent.

† The total obtained by adding the percentages of starch to 2·5 times the sum of the percentage of fat and crude proteins.

‡ Seed coats removed before analysis.

The seeds of *C. luzonicum*, from the Philippine Islands, are used in United States for dessert under the name of " pili nuts." (Cf. Pili-nut oil, *Analyst*, 1924, 49, 38.)

Carapa Oil

The exact botanical source of carapa oil is not clear, as much confusion has arisen over the different varieties of *carapa*. *C. guyanensis*, *C. toulousouna*, *C. procera*, *C. surinamensis*, *C. moluccensis* have all been described but are probably synonyms or at least only minor varieties.

The oils of *C. grandiflora*, *C. guyanensis* (*C. procera*) have been examined by Lewkowitsch (*Analyst*, 1908, 33, 184; 1909, 34, 10), who obtained the results given in the table below. The kernels of the former contained 30 per cent. of oil, those of the latter 57 per cent. of oil. The oils were found to have an intensely bitter taste. Sprinkmeyer and Diedrichs (*Ibid.*, 1912, 37, 349) examined the fat of *C. procera* which they term Tulucuna fat, whilst Bolton and Hewer (*Ibid.*, 1917, 42, 35), who emphasise the botanical confusion, have examined the fat of *C. guyanensis*, and state that the confusion is increased by the fact that they have found several specimens of Andiroba oil (the native name for carapa oil) having a rotation of 0·7 in a 100 mm. tube, whereas Lewkowitsch regards the oil of *C. procera* as being free from optically active compounds in contradistinction to the oil of *C. grandiflora*. Bolton and Hewer found 58 per cent. of oil in the kernel and 43 per cent. in the whole seed. The following characteristics have been obtained by the observers named:

Table CV.—Characteristics of Carapa Oil

Observer.	Source.	S.G. 15·5°.	Sol. Pt. °C.	M.Pt. °C.	Sap. Value.	Iodine Value.	Reichert.	Unsap. per cent.	Titre. °C.	n^{40}.
Lewkowitsch	[1] *C. grandiflora*	0·926	8	15–23	198·1	83·7	3·8	3·75	35	..
,,	[2] ,,	0·931	10	20–30	201·8	72·6	3·8	1·59	39	..
,,	[1] *C. guyanensis*	0·927	12	15–36	197·1	75·7	3·5	1·51	35	1·4623
,,	[2] ,,	0·933	14	15–48	196·4	71·3	3·1	2·04	36	..
Sprinkmeyer & Diedrichs.	*C. procera* *	..	32	38	194·8	64·9	2·3	..	..	1·4604
Bolton & Hewer . .	*C. guyanensis* †	..	..	28	197·0	62·2	2·5	0·56	36	1·4593

[1] Cold-pressed oil. [2] Hot-pressed oil.

Cashew Kernel Oil

This oil is obtained from the kernels of the cashew-nut tree (*Anascardium occidentale*, L.) which is widely distributed in the East and West Indies, notably in the Philippine Islands. This oil has been examined recently by several observers of whom may be mentioned Niederstadt, Bolton and Jesson (*Analyst*, 1915, 40, 3), Patal, Sudborough and Watson (*J.S.C.I.*, 1923, 42, 562A, 987A) and West and Cruz (*Analyst*, 1924, 49, 39). An examination of the saturated and unsaturated fatty acids by the last authors indicated that the oil was composed of oleic glyceride 80·4, stearic glyceride 17·3, and unsaponifiable matter 1·5 per cent., making a total

* Polenske, 0·5. † Polenske, 0·3.

of 99·2 per cent., whilst Patel, Sudborough and Watson found in the fatty acids oleic acid 73·8, linolic acid 7·7, palmitic 6·4, stearic 11·2, and lignoceric 0·5. The unsaponifiable matter was mainly sitosterol.

TABLE CVI.—CHARACTERISTICS OF CASHEW KERNEL OIL

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	n^{40}.	R.M.	Unsap. %	Polenske.	Titre. °C.	Acid Value
Bolton and Jesson	..	193·7	79·5	1·4623	..	..	..	..	1·6
Niederstadt . .	..	195	84	1·4629	..	..	..	..	..
Patel, Sudborough and Watson .	0·916–0·918	180–190·6	80·8–89	1·4623–1·4633	1·6	0·42	0·25	29·9	..
West and Cruz .	0·911 at $\frac{26·4°}{4°}$	187·0	85·2	1·4629	..	1·47*	..	..	..

CORNEL OIL

Cornel oil is obtained from the seeds of *Cornus sanguinea*, L., which contain upwards of 50 per cent. of a greenish-yellow oil. The oil is also called sanguinella oil and dogwood oil. The oil has been examined by De Negri and Fabris, by Grimaldi (*J.S.C.I.*, 1911, 30, 1021) and by Normann (*Ibid.*, 1919, 38, 426A), who determined various constants which are given in the table below. The last author also examined the oil from the white dogwood, the figures for which are given alongside for comparison. Cornel oil is very like olive oil in its characteristics and it may be used as an adulterant thereof. Grimaldi gives the following colour reaction for the detection of cornel oil in olive oil: warm 5 c.c. of the oil with 1 c.c. of a 1 per cent. solution of agar-agar in nitric acid (S.G. 1·4) for a few minutes and then cool; in the presence of cornel oil the oily layer is stated to become yellowish-red and the acid layer straw-yellow. This colour reaction stands in need of confirmation. The following table contains the results so far obtained. The figures of Normann are quite different from those of the other workers and need to be confirmed.

TABLE CVII.—CHARACTERISTICS OF CORNEL OIL

Authority.	S.G.15°.	Sol. Pt.	Sap. Value.	Iodine Value.	$n^{40°}$.	Titre.	Unsap. %	Acid Value.
De Negri and Fabris	0·921	−15	192·1	100·8	..	..	..	..
Grimaldi . .	0·921–0·923	−12 to −15	192·0–192·5	100–101	1·4617–1·4624	29–31	0·2	..
Normann— Fruit oil . .	..	..	192–194	115·8–195·4	1·4624–1·4660	..	1·65–2·9	4·2–37·5
Kernel oil .	..	..	193–197	143·8–147·8	1·4703	..	0·4–1·1	2·5–108
Normann— *Cornus Stolenifera* .	..	..	197	114·2	1·4659	..	..	7·8

Grimaldi states that the oil has a pleasant odour and is soluble in hot but insoluble in cold alcohol. The oil begins to solidify at 0° and becomes completely solid at −12° to −15°.

* Having iodine value 94·6.

Grape-Seed Oil

This oil is obtained from the seeds of the grape, *Vitis vinifera*, either by expression or by extraction. Large quantities of grape seeds are obtained as a by-product of the wine industries of various countries. It has been stated by G. Paris that the Italian production of grape-seed oil (*J.S.C.I.*, 1912, 31, 80) is as much as 18,000 litres per annum, whilst Shrader (*J.S.C.I.*, 1920, 39, 131A: 1921, 40, 671A) has stated that the transport of seeds to a central station for crushing purposes is a commercial proposition.

The seeds consist of some 44 per cent. shell and 56 per cent. kernel (Shrader). The kernels contain varying quantities of oil (from 10 to 30 or more per cent.) according to the kind of grapes, their method of cultivation and the time of their examination.

The colour of the oil depends very largely on the manner in which it is obtained. The oil obtained by cold expression, the edible variety, is usually of a light-yellow colour although some samples show a distinct greenish tinge, whilst oil obtained by extraction or hot expression is much darker, and has a more or less pronounced bitter taste. The oil has some drying properties as has been shown by Klinger (*Analyst*, 1921, 46, 138) who states that the oil dried to a sticky film in four days, and in a shorter time when mixed with metallic driers. The oxygen absorption was 7 per cent. in four days, whilst a control, using linseed oil, showed 14·7 per cent. On being heated to 300° the oil developed " body " more rapidly than linseed oil, and in a few hours became a gummy mass.

The composition of the oil has been studied by various workers, but there is somewhat of a difficulty at the outset. Some observers have found that grape-seed oil has a high iodine value (140) and low acetyl value (24), whilst others have found a much lower iodine value (less than 100) and an acetyl value approaching that of castor oil (140). Whether there are two distinct types of oil or whether some of the oils examined have not been authentic cannot yet be decided finally, but the results of André (*Analyst*, 1921, 46, 288) quoted below would appear to show that wide variations are possible.

G. Paris (*J.S.C.I.*, 1912, 31, 80) found that the oil contained erucic, linolic, oleic, stearic and palmitic acids, although Ulzer and Zumpfe were unable to prove the presence of erucic acid. A large amount of work has been done on this subject by André (*Analyst*, 1921, 46, 331; 1923, 48, 290; *J.S.C.I.*, 1922, 41, 639A; 1923, 42, 410A). This writer found that the only unsaturated acids in the oil were oleic and linolic, whilst stearic, palmitic and melissic acids were among the saturated acids. It would appear that ricinoleic acid is not present and that the hydroxy acids present are C_{14} or C_{16} acids, one of which is saturated and one unsaturated. Rabak (*Analyst*, 1921, 46, 500) found that the oil of the concord grape consisted of linolin 53·6, olein 35·9, palmitin 5·2, stearin 2·2.

G. Dell' Acqua (*Analyst*, 1915, 40, 54) has published some work on the colour reactions of the oil and particularly on its distinction from soya-bean oil. He states that like soya-bean oil, this oil gives a lemon yellow emulsion in the uranium nitrate test (*Analyst*, 1913, 38, 36). The oils could be distinguished, however, by heating 10 c.c. with 3 c.c. of an ethereal 2 per cent. solution of uranium nitrate for two minutes in a boiling brine-bath (102°). Soya-bean oil assumes an olive-green colour changing to garnet-red within twenty minutes, while grape-seed oil becomes yellowish-green in two minutes and golden-yellow within twenty minutes. The reactions of grape-seed oil with aqueous or ethereal solutions of uranium nitrate are not masked by the presence of a large amount of mineral oil. Hauchecorne's nitric acid test

will also distinguish between the two oils. Soya-bean oil heated for ten minutes in water at 60° with nitric acid gives an orange-brown colouration changing to chocolate-brown, while grape-seed oil assumes an orange-brown colour changing to reddish-orange.

As is the case with most other colour tests these reactions, which are apparently based on an examination of a few samples of oils, must be accepted with reserve.

The constants which have been observed by various workers are included in the table below. Paris found that the unsaponifiable matter contained a phytosterol having M.Pt. 132°–133° and $[\alpha]_D$ −32·8° of which the acetate had M.Pt. 120°–121°.

TABLE CVIII.—CHARACTERISTICS OF GRAPE-SEED OIL

Observer.	S.G. 15°.	Sol. Pt. °C.	Acid Val.	Sap. Val.	I.V.	Reichert	Acetyl. Val.	n_D^{40}.	Titre °C.	M.Pt. Acids °C.	I.V. Acids
Horn . . .	0·956	..	..	178·4	94	0·5	144·5	..	..	..	98·7
De Negri and Fabris . .	0·935	−17 to −10	..	178·5 179	95·8 96·2	..	..	..	18–20	23–25	99·0
Ulzer and Zumpfe . .	0·921	..	..	190	142·8	..	43·7	1·4657	..	..	..
Fabris and Settimj . .	0·925	−13	..	178·3	130·3	1·9	30·9	1·4671	20	25–26	132·5
Fachini and Dorta. . .	0·926	..	..	189·7 195·5	136·5 140·4	0·4	23–25	..	..	..	..
[1] Paris . .	0·950	..	16·8	179·8	96·0	..	143·1	..	..	..	..
[2] Dell' Acqua*	0·923	..	..	..	140·2	..	17·8	1·4677	18–21	25–28	141
[3] Klinger . .	0·925	..	..	192	130·9	..	..	..	18–20	23–25	133·5
[4] André . .	0·920–0·937	..	..	171·0 191·1	94·3–135·0	..	13·3–49·3	..	..	..	..
[5] Rabak † . .	0·925	−22 to −24	0·7	193·2	135·8	..	..	..	..	..	..

[1] *J.S.C.I.*, 1912, 31, 80. [2] *Analyst*, 1915, 40, 54. [3] *Analyst*, 1921, 46, 138. [4] *Analyst*, 1921, 46, 288. Examination of eleven samples. [5] *Analyst*, 1921, 46, 500. U.S.A. oil from the concord grape. About 1110 tons of the seeds are obtained annually.

* Unsaponifiable Matter, 0·32.

† Unsaponifiable Matter, 1·6.

The oil of the wild grape seed (*Vitis riparia*) has been examined by Beal and Beebe (*Analyst*, 1916, 41, 47). The crushed seeds yielded 19·4 per cent. when extracted with petroleum ether, the oil so obtained having a peculiar acrid odour and taste like those of castor oil. The acid was found to consist of 95 per cent. of liquid acids and 5 per cent. of solid acids. The oil had the following characteristics:

Specific gravity 15°	0·943
Saponification value	187·8
Iodine value	76·5
Acetyl value	61·3
n_D^{40}	1·4690
Iodine value of liquid acids	91·8

Hazel-Nut Oil

Hazel-nut oil is prepared from the seeds of the hazel-nut tree, *Corylus avellana*, the fruit of the cultivated varieties of which are known in this country as filberts. The fresh oil which is contained in the seeds to the extent of some 50–60 per cent. has a pleasant characteristic odour and taste. The oil contains 10 to 15 per cent. of solid fatty acids, most of the remainder being oleic acid. The oil resembles almond oil to a certain extent and has been used to adulterate the latter and as a substitute for peach-kernel oil. (Bennett, *C. and D.*, 1908, 89, 981.) The oil has the following characters, the iodine value being appreciably lower than that of almond oil:

Specific gravity	0·917
Sol. Point	–18
Sap. value	193–197
Iodine value	84–90
n^{40}	1·4612
Titre °C.	19–20

Colour reactions for the oil have been proposed by Schädler and by Knorr, but Jungkunz (*Analyst*, 1922, 47, 124) says that these are invalid.

The oil of the seeds of *C. rostrata Ait.* var. *Sieboldiana Maxim* has been examined by S. Higuchi (*J.S.C.I.*, 1916, 35, 262). It is known as Tsuno-hashibami nut oil. The kernels contain 46 per cent. of a colourless agreeable oil which is used by the natives as a superior edible oil. It has the following characters: S.G. 15° 0·920; acid value 0·5; sap. value 190·9; iodine value 104·6; Reichert value 3·2; M.Pt. of fatty acids 16°.

Inoy-Kernel Oil

Inoy-kernel oil is obtained from the seeds of *Poga oleosa* which grows to a considerable extent in West Africa. The kernels variously known as Njore-Njore or M'poga contain about 60 per cent. of oil, which is pale yellow in colour and which deposits a little solid matter on standing. The oil has been examined by various observers (*Analyst*, 1909, 34, 167; 1911, 36, 21) with results as set out in the following table:

TABLE CIX.—CHARACTERISTICS OF INOY-KERNEL OIL

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	n^{40}.	Titre. °C.	Acid Value.	R.M.	Unsap. per cent.
Imperial Institute .	0·896–0·918	184–193	89·7–90·9	..	22–24·5	39–45	1·45	..
Edie	0·909	188	93	..	..	..	..	..
Brieger and Kraese	0·914	193	93·3	..	..	..	..	..
Grimme . . .	0·909	177·5	91·1	1·4610	24·5	4·20	..	0·35

KOEME OIL

Koeme oil is obtained from the kernels of the seeds of *Telfairia pedata*, a plant which is abundant in East and South-East Africa, and the fruits of which are known as Jiconger nuts by the natives. The oil has a pleasant taste and odour when properly refined but the husks contain some bitter principle which is probably toxic, so that these must be removed before the oil can be used for edible purposes. No machine has yet been found which will separate the kernels so that its use on the large scale is problematical more especially as a large, regular supply is doubtful. Determinations so far made show that the kernels contain 59–63 per cent. of oil.

TABLE CX.—CHARACTERISTICS OF KOEME OIL

Observer.	S.G. 15°.	Sol. Pt. °C.	Sap. Value.	Iodine Value.	n^{40}.	Acid Value.	Unsap. Matter.	Titre. °C.
Thoms. . . .	0·918	7	..	..	1·4628	..	..	..
[1] Lewkowitsch .	..	..	195·1	100·7	1·4633	0·56	0·9	38·8
Bontoux . . .	..	..	197	88·4	..	..	..	..
[2] Grimme . .	0·919	6	186·5	84·2	1·4595 ?	2·44	0·34	41·8
[3] Bolton & Jesson	..	..	193·6	90·4	1·4623	0·31 %	..	..

[1] Lewkowitsch, *Oils, Fats and Waxes*, Vol. II, p. 333. [2] *Analyst*, 1911, 36, 21. [3] *Ibid.*, 1915, 40, 3.

The oil of the seeds of *T. occidentales* has been examined by C. Grimme (*Analyst*, 1911, 36, 22). The kernels contained 48 per cent. of a thick viscous oil with fairly good drying properties having the following characters: S.G. 50°, 0·914; M.Pt. −1°; n^{40} 1·4690; acid value 61·5; saponification value 262·2; iodine value, 43·4; unsaponifiable matter 0·38 per cent.; titre 39·5°.

MOROCCAN OLIVE OIL

Argan Oil

At one time the so-called "Moroccan olive oil," which had a considerably higher iodine value than ordinary olive oil, was considered to be a variety of the latter. A number of true olive oils from olives grown in Morocco were,

however, examined by Sasserath, who found that the iodine values were quite normal. He then found that the oils previously known as " Moroccan olive oil " were derived from the fruits of *Arganum sideroxylon* which has the following characteristics (*Analyst*, 1911, 36, 107). A characteristic dark crimson colour is said to be developed on shaking the oil with nitric acid (S.G. 1·4).

S.G. 15°	0·919
Sap. value	192·1
Iodine value . . .	95·9
R.M. value . . .	1·8
Acid value	0·18

Olive-Kernel Oil

Olive-kernel oil is prepared from the kernels of the fruit of the olive tree *Olea europea*. In some cases the kernels are crushed with the fruit, but in other cases the kernels are removed and pressed separately—they contain upwards of 25 per cent. of oil. The oil resembles almond oil in its appearance and properties, but its iodine value is lower and it gives a distinct kernel oil reaction in the Bieber test. Klein has found the following range of figures of genuine oils:

Specific gravity at 15·5° .	0·918–0·919
Saponification value* . .	181·2–183·8
Iodine value	87·0–87·8
n^{40}	1·4618–1·4634

Queensland Nut Oil

Macadamia-nut oil obtained from the Macadamia or Queensland nut (*Macadamia ternifolia*) and it is stated by A. and F. R. Morrison (*J.S.C.I.*, 1924, 43, 915B) to resemble closely the best olive oil. A yield of 44 per cent. is obtained by expression of the kernels, whilst extraction yields 73–76 per cent. No deposit is obtained above 0°, whilst its solidification-point is −12°. C. A. Lathrop (*J.O.F.I.*, 1925, 2, 44) considers that the oil may become of commercial importance as it would make a bland and delicious salad oil whilst the nuts themselves make a delicate table nut. The fatty acids consist of oleic acid with small quantities of palmitic and stearic acids. The following characters have been observed:

Observer.	S.G. 15°.	Sap. Value.	Iodine Value.	n^{40}.	Acid Value.	Unsap. per cent.
Lathrop	0·914	193·7	74·2	1·4609	0·22	0·32
A. and F. R. Morrison .	0·912–0·915	195·6	74·5–75·8	1·4602	0·11	0·1–0·2

Rice Oil

Rice oil is obtained to a certain extent by expression of Rangoon rice meal (*Oryza sativa*) which contains about 15 per cent. of oil. The oil has a dirty greenish colour and frequently a high acid value on account of enzyme

* Evers, in a private communication, gives 190.

action which has taken place in the seed before expression. According to Lewkowitsch, oil from fresh rice bran is practically neutral.

Tsujimoto (*Analyst*, 1911, 36, 357) found that the fatty acids of the oil consisted of palmitic 20 per cent., oleic 45 per cent., isolinolic acid 25 per cent. The phytosterol had M.Pt. 136°–137°.

Davidson (*J.S.C.I.*, 1914, 33, 651) found that on keeping a solid fat, M.Pt. 46°, separated from rice oil. The characters of the residual liquid oil (water 0·32 per cent.) and of the solid fat (water 0·43 per cent.) were as follows:

	Sp. Gr. at 15°.	Butyro-refrac. Reading.	Acid Value.	Sap. Value.	Iodine Value.	Saponifiable Matter.
						%
Oil . .	0·918	67·8 (25°)	98·56	198·44	108·5	99·47
Fat . .	0·924	44·7 (50°)	124·30	197·21	74·11	99·43

The following characteristics have been observed:

TABLE CXI.—CHARACTERISTICS OF RICE OIL

Observer.	S.G. 15°.	Acid Value.	M.Pt. °C.	Sap. Value.	Iodine Value.	n_D^{40}.	Titre. °C.	M.Pt. Acids. °C.	I.V. Acids.	Unsap. per cent.
[1] Smetham	..	86–154	29	192·0–195·8	96·4–99·9	..	..	..	..	..
[2] Browne .	..	..	..	193·5	91·7	..	..	..	..	..
Fabris and Settimj	0·923	..	..	..	106·5	1·4658	28–29	31–32	109	..
Tsujimoto	0·927	34·8	..	184·9	107·6	1·4669	..	30·5	109·5	4·8
[3] Garelli .	0·918	[4] 90 [5] 13·8	25–26 ..	186 179·4	99·7	..	..	..	..	3·2 0·7

[1] *Analyst*, 1893, 18, 191. [2] *J.S.C.I.*, 1903, 22, 1137. [3] *Analyst*, 1918, 43, 141. [4] Extracted with petroleum spirit. [5] Expressed oil.

Saké oil consists chiefly of rice oil and is found floating on the surface after the fermentation of saké, a Japanese fermented drink prepared from rice. The oil, which is an orange-yellow liquid with an odour of saké has been examined by Tsujimoto (*J.S.C.I.*, 1915, 34, 1259) with the following results:

Specific gravity 15°/4° .	0·903
Solidification point . .	Turbid at 0°
Acid value	22·6
Saponification value . .	179·1
Iodine value	101·6
n_D^{40}	1·4587

For information on the composition of rice, see *J.S.C.I.*, 1917, 36, 159; 1918, 37, 601A; *Analyst*, 1920, 45, 451.

Pistachio Oil

This oil is obtained from the seeds of *Pistacia lentiscus*, L., a small tree indigenous to the Mediterranean and grown particularly in Cyprus. The resinous exudation of this tree is the mastic of commerce. The oil is used to a certain extent in the manufacture of confectionery as a flavouring agent—the extracted oil being preferable for this purpose on account of the greater amount of aromatic substances obtained in this way. The expressed oil, after prolonged boiling with water, is used as an edible oil in Sardinia. The non-volatile acids are stated by Sernagiotto and Vita (*J.S.C.I.*, 1915, 34, 1061) to consist entirely of palmitic and oleic acids. The following characteristics have been observed in the fixed oil after removal of the volatile matter:

Table CXII.—Characteristics of Pistachio Oil

Observer.	S.G. 15°.	Sap. Val.	Iodine Val.	n^{40}.	Titre °C.	Acid Val.	Sol. Pt. °C
De Negri, Fabris & Setting.	0·919	191·5	86·8–92·5	1·4617	13	..	−9
Sernagiotto and Vita . .	0·919	165·6	83·6	1·4603	..	15·9	..

Sejen-Nut Oil

This oil which is obtained from the nuts of the " sejen " or " unamo " palm (*Jessenia polycarpa*, Karst) has been described by Bacharach (*Analyst*, 1918, 43, 289), who states that it has a reputation in the plains of San Martin both for chest and lung complaints and for culinary purposes.

The oil is a pale yellow liquid having (in the samples examined) a slight fluorescence and a not unpleasant smell. Some " stearine " is deposited in cold weather. The oil behaves in the elaidin test in a similar manner to olive oil. The oil is miscible in all proportions with the usual fat solvents but not with alcohol or glacial acetic acid. Bacharach obtained the following figures on the examination of three samples:

Table CXIII.—Examination of Sejen-Nut Oil (Bacharach)

	I.	II.	III.
Specific gravity 15°/4°	..	..	0·9161
Refractive index n_D^{20}	1·4682	1·4682	1·4682
Saponification value	190·5	189·5	188·5
Acid value	4·0	3·8	3·8
Iodine value (Wijs)	73·5	74·8	74·1
Hehner value	..	..	93·8
Molecular weight of insoluble fatty acids .	..	..	273
Iodine value (Wijs) of free fatty acids . .	..	..	79·5

Tea-Seed Oil

Chinese tea-seed oil is expressed from the seeds of a tea plant (*Thea asanqua*, Nois) which is specially cultivated as an oil-bearing plant in China and adjacent countries. The commercial tea-seed oil may be obtained from Chinese Assam or Japan and may be from many varieties of *Thea*. The oil is used locally as an edible oil (Lewkowitsch considers that the proportion of saponin present may render the expressed oil somewhat unsafe for consumption; the extracted oil contains no saponin) and has been used to a considerable extent as an adulterant of olive oil. Oils from various sources have been examined by different observers, and their results are given in the following table. Commercial tea-seed oils may consist of any of these oils or of mixtures of two or more. Bieber's reagent is said to give a bright bluish-green colouration; the oil from *Thea paponiea* is known as Tsubaki oil and that from *Thea sasanqua* as Sasanqua oil.

Table CXIV.—Characteristics of Tea-Seed Oil

Authority.	Source.	S.G. 15° C.	Sap. Value.	Iodine Value.	I.R. 40°.	Acid Value.	R.M.	Sol. Pt. °C.	M.Pt. Fatt Acid °C.
Tsujimoto * . .	*T. sinensis*	0·918	191·9	90·4	1·4634	0·74	0·7	−10	33·5
Menon . . .	,,	0·903	189·9	92·7	..	..	0·6	..	38·9
Uchida † . . .	*T. chinensis*	0·913‡	193·8	86·2	1·4624	4·12	0·1	..	25·5
Bull. Imp. Inst. .	*T. sasanqua*	0·918	193·4	87·5	..	9·4	..	..	..
Tsujimoto . .	*T. sasanqua*	0·916	193·4	81·7	1·4619	6·8	1·2	−9	28
		0·919	193·9	82·3	..	..	..	..	..
Cofman-Nicoresti	Commercial oils	0·197–0·920	179·5–189·4	80·1–92·7	..	..	..	..	..
Tsujimoto ‖ . .	*T. japonica*	0·916	190·6¶	80·3	1·4609	..	..	..	..
		0·917	192·6	81·3	1·4618	..	..	0·5	22
Higuchi . . .	*T. sasanqua*	0·915	193·3	81·4	..	7·7	0·35	..	22
Higuchi . . .	*T. japonica*	0·916	196·1	80·9	..	4·6	0·4	..	..
Nakatogawa and Kobayashi . .	*T. japonica*	0·915	190·3	77·3	1·4613	1·8	..	..	..
		0·916	192·6	81·1	1·4623	7·6	..	..	..

Various colour reactions have been suggested for the detection of tea-seed oil in other oils but their utility is doubtful and great care should be taken before an olive oil is pronounced as adulterated with tea-seed oil.

Cofman-Nicoresti (C. and D.) states that the oil gives no colour with the Halphen or Baudouin reactions. He proposes a test for the oil which is as follows: Shake 10 c.c. of the oil with 10 c.c. of a mixture of equal weights of conc. nitric acid, conc. sulphuric acid and water and heat for 20 minutes in boiling water. With not less than 20 per cent. of tea-seed oil the oily layer becomes pink. It is suggested that an adulteration with 10 per cent. may be detected by adding a further 10 per cent. when a faint colour will be produced with the 20 per cent. of tea-seed oil then present.

* *Analyst*, 1908, 33, 424.
† *J.S.C.I.*, 1916, 35, 1093.
‡ At 30°.
§ Soluble point, Titre test.
‖ *J.S.C.I.*, 1908, 27, 454.
¶ Commercial oils gave saponification values 181–190·6.

Dybowsky and Millia (*Analyst*, 1921, 46, 458) state that " The presence of 10 to 20 per cent. of tea-seed oil in olive oil may be detected by shaking 20 grms. of the oil for one minute with 6 drops of sulphuric acid; the mixture is then treated with 9 drops of nitric acid, shaken for one minute, heated at 100° for five minutes, and finally cooled to 10°. After two hours at the latter temperature the mixture remains liquid if 20 per cent. of tea-seed oil is present; if the original oil contained 10 per cent. of tea-seed oil the mixture solidifies, but the mass is not as hard as that obtained with pure olive oil. A characteristic reaction, which will detect as little as 5 per cent. of tea-seed oil, consists in shaking 4 c.c. of the oil for thirty seconds with a mixture of 5 c.c. of pure sulphuric acid, 3 c.c. of nitric acid, and 3 c.c. of water; the whole mixture is kept at 5° for five minutes and observed after a further fifteen minutes. Pure olive oil gives a straw colouration and remains clear, pure tea-seed oil becomes turbid and sooty-black, whilst olive oil containing 5 per cent. of tea-seed oil gives a dark straw-coloured, turbid mixture. These colourations are observed in the oily layer; the acid layer is colourless in all cases."

Mitchell (*loc. cit.*) however, considers that the tea-seed oil giving these reactions had probably not been refined, and Sutcliffe is of opinion that the oil can generally be refined so as to give no colour with any of the tests that have been suggested, an opinion with which the author is in entire agreement. Tea-seed oil cannot be used without deodorising so that an olive oil tasting of deodorised oil may be suspected of containing tea-seed oil.

CHAPTER XVII

ALMOND OIL AND SIMILAR KERNEL OILS

Almond Oil

Source.—Almond oil is obtained principally from the bitter almond (*Prunus amygdalus*, var. *amara*) although sweet almonds (*Prunus amygdalus*, var. *dulcis*) are occasionally used and also, rather more frequently, a mixture of the two. The almond is cultivated in Southern Europe, Northern Africa, Syria and Persia. The bitter almond usually contains about 45–55 per cent. of oil, of which about 38–45 per cent. is yielded under normal conditions. Sweet almonds on the average contain more oil than bitter almonds, with a consequent greater yield on pressure. Rosenthaler (*J.S.C.I.*, 1923, 42, 233A) finds the oil content of sweet almonds from 55·3–60·5 per cent., the larger seeds containing the least oil, whilst the bitter almond contained from 35·5–62·5 per cent. (73 per cent. of the samples varied between 45 and 55 per cent.) with practically no relationship between percentage of oil and size of seed. According to Lewkowitsch the amount of oil in bitter almonds may fall as low as 20 per cent.

Bitter almonds contain a glucoside amygdalin and an enzyme emulsin.* Under suitable conditions the glucoside will decompose under the influence of the emulsin with the production of glucose, hydrocyanic acid and benzaldehyde. The press cake is therefore allowed to stand with warm water and the product steam distilled with production of essential oil of almonds. Bitter almonds yield about 0·5-0·8 per cent. of essential oil which contains as a rule from 4 to 7 per cent. of hydrocyanic acid. No amygdalin is contained in sweet almonds.

Composition.—The fatty acids consist very largely of oleic acid, but some linolic acid is also present as shown by the iodine value; Farnsteiner isolated 5·8 per cent. Stearic acid has been considered absent by Gusserow and by Hehner and Mitchell (cf. Ross and Race, *Analyst*, 1911, 36, 263). Contrary to earlier statements to the contrary almond oil does not readily turn rancid on keeping, this may be due to the comparative absence of highly unsaturated fatty acids. Jensen has found oils with acid value as high as 15·4 which showed no indication of rancidity. There is apparently practically no difference between the oils from bitter and from sweet almonds.

Properties and Special Tests.—Almost colourless to pale yellow with a pleasant taste, described by the B.P. as bland and nutty. The special tests and properties of almond oil depend on the fact that this oil is practically free from solid glycerides and that, as has been shown above, it consists very largely of oleic glyceride. For this reason it should not become turbid on standing for three hours at −10° as required by the B.P., and further, it should not solidify above about −18°. The mixed fatty acids should dissolve to a clear liquid in an equal volume of alcohol at 15° and the addition of a further similar volume of alcohol should produce no precipitate.

Examination for Adulteration.—Almond oil is not often adulterated in late years by the addition of large quantities of the common vegetable oils on account of the comparative ease with which these can be detected by

* Cf. Tonegutti (*J.S.C.I.*, 1911, 30, 221).

TABLE CXV.—ANALYTICAL CHARACTERS OF ALMOND OIL

Authority.	S.G. 15°/15°.	Ref. Index * 40°.	Iodine Value.	Acid Value.	Sapon. Value.	Sol. Pt. °C.	M.Pt. °C.
Evan's Annual Reports .	0·916 0·9175–0·9195	(1·4612–1·4642) 1·4626–1·4639	(95–103) 97·2–101·7	0·8–4·8	..	..	..
Fryer and Weston . .	0·9178–0·9183	1·4634–1·4643	98–100	0·5–5·0	189–193	9·5–12	..
Mitchell	0·9175–0·9195	1·4637	93–101·5	..	189·5–192	9·5–11·8	13–14
B.P.	0·915–0·920	1·4624–1·4640	93–100	not 6	188–196	..	..
U.S.P.	0·916–0·921	..	93–100	..	191–200	11·3–11·8	14
Lewkowitsch	0·9178–0·9200	1·4636–1·4643	96·7–100·2	0·8–5·2	183·3–195	9·5–11·8	..
Southall's Annual Reports .	0·916–0·920	1·4618–1·4631	98·4–99·5	..	190·8–192·5	..	..

* Harvey, 1·4629–1·4637.

means of the ordinary analytical figures and by the special tests mentioned above. The most likely adulterant is apricot-kernel oil (q.v.) or one of the other kernel oils which are closely allied with this. Adulteration with these oils is practised to a considerable extent, in fact, complete substitution not infrequently takes place. These kernel oils are often sold as " almond oil, Persic " or " oil of sweet almonds, French." This substitution is not looked upon as serious by some, but the expensive nature of almond oil renders the exchange a profitable one and it should undoubtedly be looked upon as serious adulteration.

Where adulteration with these kernel oils takes place it is usually with a large proportion, which is a fortunate occurrence as the detection of small proportions is practically an impossibility. Large admixtures or complete substitution may be detected by the colour tests given under apricot-kernel oil or by the increase in the iodine value. The matter, however, is one of some difficulty and care and experience are necessary in drawing conclusions, as some almond oils give very faint positive indications with the colour tests. Beech-nut oil, page 197, has been suggested as a possible adulterant.

The important tests are the solidifying-point of the oil, as already mentioned above, and the iodine value. The iodine value is very rarely more than 100 and certainly any figure above this must be looked upon with grave suspicion, especially if a positive result is obtained with one of the colour tests for kernel oils. An oil with an iodine value of 102 or over must be considered to be definitely adulterated. In such cases the various results must be carefully compared both among themselves and with those of oils of known purity.

The acid value should not be more than 5·0 and is usually much less than this although samples with an acidity as high as 9·2 per cent. of oleic acid have been found by Umney to be free from objectionable odour and taste even after standing for a further six months. Some oils (one with high acidity) were found by Jensen (Evans, Sons, Lescher and Webb, *Analytical Notes*, 1913, 8, 6) to give a turbidity with Bellier's qualitative test as modified by Evers (page 260). The oils were, however, considered to be pure. The Reichert value is given by Ross and Race as 2·6 with a Polenske value of 0·6 but this figure would appear to be much too high. The Reichert value is usually 0·0–0·3 and the Polenske 0·2–0·6, the latter sometimes rising as high as 1·0. (Cf. *Y.B.P.*, 1913, 573; *Analyst*, 1924, 49, 180.)

References.—Lewkowitsch, *Analyst*, 1904, 29, 105. Harvey, *J.S.C.I.*, 1905, 24, 717. Thomson and Dunlop, *Analyst*, 1906, 31, 282. Ross and Race, *ibid.*, 1911, 36, 263. Umney, *J.S.C.I.*, 1914, 33, 556. Cf. *The Kernel Oils of the Cherry, Apricot, Plum and Peach.*

Apricot-Kernel Oil

Source.—Apricot kernel oil is obtained from the kernels of *Prunus armeniaca* L. The commercial " Almond oil, French " or " Almond oil, Persic " consists either of pure apricot-kernel oil or a mixture of this oil with peach-kernel oil or of peach-kernel oil alone. The apricot kernels are frequently mixed with peach kernels before the oil is expressed. Apricot kernels contain some 40–45 per cent. of oil. The commercial oil is obtained from sweet kernels; a somewhat inferior oil in taste is sometimes prepared from imported Japanese bitter kernels.

Composition.—The exact character of the fatty acids contained in the oil does not appear to have been determined, but from a comparison of its pro-

perties with those of almond oil it would appear that the oil is very similar in composition. The oil is pale yellow in colour and in appearance and taste closely resembles almond oil, but most observers have agreed that the iodine value is higher. Umney found that 34 samples gave a range of acidity of from 0·6 per cent. to 5·97 per cent. expressed as oleic acid and he states that the oil with high acidity was very unsatisfactory as regards odour and taste after keeping for a year in contradistinction to almond oil (q.v.).

Table CXVI.—Analytical Characters of Apricot-Kernel Oil

Authority.	S.G. 15°/15°.	Ref. Index 40°.	Iodine Value.	Sap. Value.	
Lewkowitsch	0·917–0·920	1·4639–1·4646	107·4–108·7	190·3–198·2	
Ross and Race	0·920	1·4639–1·4649	100–106	184–192·4	
C. A. Hill	..	..	100–110	..	
Southall's Annual Reports	0·916–0·920	1·4609–1·4629 *	100·3–105·3	190·1–191·7	
	15°/4°.				
Ueno	0·919	1·4650	105·4	188·6	Mongolian kernels
	0·910	1·4586	90·4	182·3	Chinese kernels R.M. = 0·7

Properties and Special Tests.—The properties of apricot-kernel oil are very similar to the other kernel oils which are all closely allied to almond oil. The solidification-point of the oil is at least as low as that for almond oil, whilst the solidification-point of the fatty acids and their melting-point are even lower. The Reichert and Polenske values are similar to almond oil (q.v.). These properties will serve to distinguish the oil from vegetable oils in general whilst the somewhat higher iodine value will distinguish the oil from almond oil taken in conjunction with the colour tests now to be described.

Bieber's Test.—Prepare the reagent by mixing together equal weights of water, sulphuric acid and fuming nitric acid. Mix thoroughly 1 c.c. of this reagent with 5 c.c. of the oil and then allow to stand for a few moments at ordinary temperatures. The reagent should be prepared freshly for each test. Almond oil gives no change in colour, apricot-kernel oil gives a pink colour as also do peach kernel and plum kernel, although to a lesser extent. The conclusions arrived at must be accepted with a certain amount of reservation, and considerable experience is necessary before anything like certain conclusions can be drawn. The test is practically useless as a colorimetric one for quantitative purposes on account of the different depths of colour produced by oils from different sources. Ross and Race found that the reaction was still given strongly by oils that had been steamed for some hours and even after keeping for a year and bubbling air through the warm oil for three days. Lewkowitsch found that the reaction was given more

* These figures are for mixed apricot and peach-kernel oils. They are given as 1·4700–1·4721 at 15·5°, but they seem abnormally low.

strongly by a freshly-prepared oil than by an older one; this observer also found that 25 per cent. of apricot-kernel oil in almond oil could not be detected with certainty.

The Kreis Phloroglucinol Test.—This test proposed by Kreis and modified by Chwolles and Lewkowitsch consists in shaking the oil with an equal quantity of a mixture of equal volumes of one-tenth per cent. phloroglucinol in ether and nitric acid S.G. 1·45. Kernel oils give a deep red colouration, whilst some almond oils do not. The fact, however, that some almond oils of undoubted purity give a more or less marked reaction make this test more uncertain than that of Bieber.

Nitric Acid Test.—Nitric acid of S.G. 1·4 on shaking with apricot-kernel oil or other kernel oil assumes a much deeper tint than it does with almond oil where the mixture becomes at most pale yellow.

Nickle's Reaction.—This test, which is recommended by De Negri and Fabris, consists in shaking the oil with calcium hydroxide. Apricot-kernel oil gives a permanent emulsion, whilst most vegetable oils such as almond, olive, etc. remain clear.

Examination for Adulteration.—Apricot-kernel oil, although used as a substitute or an adulterant for almond oil, is itself liable to sophistication. Various seed oils may be used for this purpose, but the practice is not nearly as common as it used to be. The solidifying-point and the iodine value are the two important tests. The remarks under the adulteration of peach-kernel oil should be read in this connection.

References.—Lewkowitsch, *Analyst*, 1904, 29, 105. Ross and Race, *ibid.*, 1911, 36, 263. Umney, *J.S.C.I.*, 1914, 33, 556. Cf. *Evans' Annual Reports* for several years between 1907 and 1914. Ueno, *J.S.C.I.*, 1918, 37, 707A.

Cherry-Kernel Oil

Cherry-kernel oil is obtained from the kernels of the cherry (*Prunus cerasus*, L.) large quantities of which are available from the manufacture of cherry liqueurs in South Germany where the cold-drawn oil is used for edible purposes. The kernels contain from 35–39 per cent. of oil which when obtained by extraction contains some hydrocyanic acid. Maxwell (*J.S.C.I.*, 1918, 37, 214A) states that the extracted meal contains amygdalin.

With nitric acid (S.G. 1·4) the oil assumes a dark-reddish-brown colour, whilst with Bieber's reagent a brown colouration is obtained. Lewkowitsch states that the oil is not used as an adulterant of almond oil on account of the ease with which it becomes rancid, but it does not seem likely that all unscrupulous vendors will be unduly worried with what happens to an oil when once it is sold. In any case, the iodine value will distinguish it fairly sharply from almond oil.

Kernel oils in general are prepared in some such way as the following (Alpers, *J.S.C.I.*, 1916, 35, 931): "The cracked stones of fruits such as cherries, plums, apricots, etc., are treated with a solution of chloride of calcium or magnesium of about 1·15 sp. gr. The shells sink to the bottom, and the kernels are skimmed off the surface of the liquid, washed, dried, and the oil expressed. Only traces of hydrocyanic acid can be formed by cyanogenetic enzymes, since amygdalin is only sparingly soluble in such salt solutions; but to prevent risk it is advisable to renew the solution frequently. Oil thus prepared from plum-stone kernels had the taste and odour of bitter almonds, but it was rendered nearly odourless by exposure

to a current of steam. The same effect was also obtained by heating the oil to 160°, or by exposing it to the air for fourteen days. The distillate from the treatment of 100 grms. of oil with steam contained 4 mg. of hydrocyanic acid."

The following constants have been determined by various observers. They mostly refer to extracted oils.

TABLE CXVII.—CONSTANTS OF CHERRY-KERNEL OIL

Observer.	S.G. 15°.	Sol. Pt.	Sap. Value.	Iodine Value.	Titre. °C.	M.Pt. Fatty Acids.	n^{40}.
De Negri and Fabris.	0·924	−20	195	110·8	13–15	19–21	..
Micko	0·929	..	193·4	114·3	..	16–21	..
Tortelli and Ruggeri	..	..	..	113·2	..	..	..
Maxwell	0·922–0·925	−20	202·5	..	..	..	..
Alpers	0·922–	..	192·1	111·6	..	..	1·4697–
	0·925	..	197·8	122·6	..	..	1·4713

PEACH-KERNEL OIL

Peach-kernel oil is obtained from the kernels of the peach (*Prunus persica*). Commercial peach-kernel oil is frequently apricot-kernel oil (q.v.) or may be a mixture of the two oils. These two oils are very similar, the chief difference being that peach-kernel oil gives a much less strongly-marked reaction in the Bieber test than does apricot kernel—in other ways it behaves exactly as this latter, the article on which should be read in connection with peach-kernel oil. Peach-kernel oil has been adulterated with poppy-seed oil and has been substituted (Bennett, *C. and D.*, 1908, 89, 981) by hazel-nut oil (q.v.). The observed constants of the oil are very similar to those of apricot-kernel oil, in fact, there is some confusion between them. The following may be taken as usual figures:

S.G. at 15°	0·918–0·921
Sol. Pt.	Below −15
Saponif. value	189–192·5
Iodine value	100–110 (usually 105 or more)
n^{40}	1·4639–1·4650
Titre test	13

PLUM-KERNEL OIL

Plum-kernel oil is obtained from the kernels of plums (*Prunus domestica*, L. and *Prunus damascœna*, L.). The oil is similar to almond oil and the other kernel oils in appearance. It responds to the Bieber test to a considerable extent giving a well-marked pink colouration and an orange colour with nitric acid (S.G. 1·4). The oil is prepared from the kernels as described under cherry-kernel oil on page 254. The oil has been examined by several observers and particularly in more recent years by Kassner and Eckelmann (*J.S.C.I.*, 1915, 34, 668), Fordyce and Torrance (*Analyst*, 1919, 44, 238), Utz (*J.S.C.I.*, 1919, 38, 505A), and Alpers (*J.S.C.I.*, 1919, 38, 729A), with results as set out in the following table:

TABLE CXVIII.—CHARACTERISTICS OF PLUM-KERNEL OIL

Observer.	S.G. 15°.	Sol. Pt. °C.	Sap. Value.	Iodine Value.	n^{40}.	Titre. °C.	Acid Val.
De Negri and Fabris and Settimj . .	0·919	−5 to −10	189·1–191·5	91·2–100·4	..	12–15	..
Micko	0·916	..	191·6	100·2	..	..	..
Tortelli and Ruggeri .	..	..	..	93·3	1·4624	..	..
Kassner & Eckelmann*	0·916	..	188·1	104	..	..	1·44
Utz and Alpers . .	0·919–0·921	..	188–198·5	103·6–121·1	1·4637–1·4647	..	..

* Oil from prune kernels. The kernels contained 1·82 per cent. of amygdalin.

CHAPTER XVIII

ARACHIS OIL

SOURCE.—Arachis oil is obtained from the kernels of the nuts of *Arachis hypogæa* which is apparently a cultivated variety of the plant originally a native of Brazil. The plant is a creeping herb, the flowers forming in the axes of the leaves. The fruit buds grow down into the earth where the fruit is ripened forming the nuts of commerce. The nuts are variously known as arachis-nuts, pea-nuts, earth-nuts, ground-nuts and monkey-nuts. It is cultivated in various parts of the world, the principal districts being Japan, India and further India, West Africa, South America, parts of U.S.A., the West Indies and China. The oil is largely expressed in the South of France. A large proportion of the nuts are decorticated before shipment and the oil obtained from this source is inferior, on account of the fact that the nuts undergo " heating " during the voyage, and cannot be used as a fine edible oil although the less inferior oils may sometimes be used as a second-grade edible oil.

The nuts contain about 35 per cent. of oil, the kernels about 50 per cent., the yield on the large scale is about 28 per cent. on the nuts or 45 per cent. on the kernel, but those from some districts yield less than this, e.g., the nuts from La Plata only yield about 28 per cent. of oil; on the other hand some samples have yielded over 50 per cent. (*J.S.C.I.*, 1919, 38, 871A). The oil is usually pressed in two or three stages, that with the finest flavour being produced by the first pressing in the cold (yield about 18 per cent.). The second pressing is carried out at about 30, the oil thus produced being used as a second-grade edible oil or as a burning oil, whilst the third pressing at about 50°–60° produces a somewhat thicker and more turbid oil, which is used for soap-making or as a lubricant. Before pressing the nuts are decorticated and the red brown skin which covers the kernel is removed as far as possible by means of a violent current of air. The lower qualities of the oil are refined with soda and ammonia (Bouchard, *J.S.C.I.*, 1914, 33, 428). From the ammonia treatment a paste-like deposit is produced which is treated with mineral acid to give " Arachis oil No. 2," which is used for soap-making. An account of the losses taking place during refining is given by Thurman (*J.S.C.I.*, 1923, 42, 561A) and by Holde (*J.S.C.I.*, 1923, 42, 896A), who state that the average loss is 1·57 per cent., one-third of which is in the bleaching; this figure is supported by Schadler (*Technologie der Fette*, 1, 518), who gives 1·5. The oil is finally usually filtered over charcoal or fuller's earth.

Composition.—Arachis oil does not readily yield a stearine, but if it is allowed to stand for a long time in the cold a more or less solid body can be produced, known on the Continent as " margarine d'arachide," which melts at just over 20° and has an iodine value below 80. The characteristic acids of arachis oil are arachidic and lignoceric acids on the presence of which the tests for distinguishing the oil depend. The presence of palmitic acid was reported by Caldwell but denied by Kreiling, recent work, however, has shown that it is present. The " stearic acid " found by Hehner and Mitchell (*Analyst*, 1896, 21, 328) has been shown by Meyer and Beer

(*Analyst*, 1913, 38, 514) to be a mixture of arachidic and lignoceric acids, but nevertheless this acid is apparently present. A certain amount of controversy has ranged round the supposed presence of hypogæic acid in the oil, many of the earlier investigators having reported the finding thereof. The later investigators mentioned below and that of Meyer and Beer (*vide supra*) seem to prove definitely that this acid is not present. The composition of the oil has been dealt with at length by Heiduschka and Felser (*J.S.C.I.*, 1920, 39, 272A), who find that the mixed fatty acids contain arachidic acid 2·3 per cent.; lignoceric acid, 1·9 per cent.; stearic acid, 4·5 per cent.; palmitic acid, 4·0 per cent.; oleic acid, 79·9 per cent.; and linolic acid, 7·4 per cent. Hypogæic and behenic acid they found to be absent. The composition has also been studied by Jamieson, Baughman and Brauns (*Analyst*, 1921, 46, 457), who agree entirely with Heiduschka and Felser in regard to the qualitative composition, but show considerable variation in the amounts of the individual acids present. They found that Virginian and Spanish nuts gave slightly varying results, the average composition being oleic acid, 56·7; linolic acid, 23·1; palmitic acid, 7·3; stearic acid, 5·5; arachidic acid, 3·6; lignoceric acid, 2·9. Heiduschka and Felser reply (*J.S.C.I.*, 1922, 41, 674A), but further discussion of the problem would not appear to be valuable until the technique of the separation of fatty acids has been placed on a more sure basis. Myddleton and Barry (*Fats: Natural and Synthetic*, London, 1924, page 107) found in a sample of arachis oil: palmitic acid, 8·5; stearic acid, 6·0; arachidic acid, 4·9; lignoceric acid, 3·0; oleic acid, 51·6; linolic, 26·0; which results agree fairly well with those of Jamieson, Baughman and Brauns as against those of Heiduschka and Felser. The qualitative composition seems to be definitely settled but the quantitative composition (which will doubtless vary with different varieties of oil) is still somewhat uncertain.

The composition of the proteins has been investigated by Johns and Jones (*J.S.C.I.*, 1917, 36, 158, 732), who conclude that the cake would be very suitable to supplement cakes deficient in basic amino acids. The cakes " keep " as well as ordinary cake (*Analyst*, 1918, 43, 63).

Hydrogenated Arachis Oil.—Myddleton and Barry (*loc. cit.*) give the composition of the fatty acids of a hardened arachis oil of iodine value 25·9 (iodine value of original oil, 89·9) as palmitic 8·5; stearic, 32·6; arachidic. 4·9; lignoceric, 3·0; oleic, 23·0; linolic, 0·0; new acids of hydrogenation, 28·0.

Properties and Special Tests.—The colour of arachis oil varies from pale yellow to light brown. The best qualities have a bland nutty flavour which is quite pleasant and which makes them a satisfactory edible oil. The oil is used as a salad oil and for packing tinned fish, for which purposes it served excellently as a substitute for olive oil but, of course, there should be no implication either directly or indirectly that the more valuable oil has been used. The oil has excellent keeping properties and does not easily become rancid. The Livache test gives an absorption of about 2·5 compared with about 15 for linseed oil. There are no special colour tests for this oil, its detecting and determination in mixtures depending upon the isolation of " arachidic acid." The " arachidic acid " so produced is in reality a mixture of arachidic and lignoceric acids, but the shorter term will be used here for convenience. The determination of arachidic acid is dealt with fully in the next paragraph, but it is not usually necessary to do this on every occasion when testing olive oil or other oils for arachis oil. A qualitative test has been devised by Bellier and modified by Mansfeld, Adler and Franny and Evers which gives excellent results. This test has been adversely criticised by

TABLE CXIX.—ANALYTICAL CHARACTERS OF ARACHIS OIL

Authority.	S.G. 15°/15°.	Ref. Index 40°.	Iodine Value.	Sap. Value.	Titre Test. °C.	Acid Value.	R.M. Value.	Unsap. per cent.	Sol. Pt. °C.
Lewkowitsch . . .	0·918	..	90·2	..	28·1–29·2	..	..	..	..
B.P.	0·916–0·921	1·4628–1·4645	83–101	190–196	28–30	Not more than 6	..	..	..
Leach	0·917–0·921	..	83–103	190–196	29·2	..	..	0·54–0·94	−3 to 0·0
Mitchell	0·917–0·926	..	92–100·8	185·5–196	25–32	..	0·5	..	..
Fryer and Weston . .	0·916–0·918	1·4626–1·4643	88–95	191–196	28–29	Average 10. Not usually over 20	0·5	1·0	..
Evans' Annual Reports .	0·916–0·919	1·4617–1·4634	82–90 and up to 100	186–200	28–32 M.Pt.	1·2–8 and up to 30	..	..	..

Lewkowitsch and some oils, such as " residuum olive oils," do certainly give slight positive reactions although free from arachis oil. This only means, however, that a positive result must always be confirmed by means of a quantitative determination (which would presumably always be done whether the test were absolutely specific or not) and does not interfere with the deduction that an oil not giving the qualitative reaction certainly contains less than 5 per cent. of arachis oil. The qualitative test as finally modified by Evers may be carried out as follows: One c.c. of the oil is saponified with 5 c.c. of alcoholic potash (85 grms. potash dissolved in 80 c.c. of water and diluted to one litre with industrial methylated spirits), 1·5 c.c. of acetic acid of such a strength as to exactly neutralise the alcohol potash is added (about 1 volume of glacial acetic acid to 2 volumes of water), and the tube cooled in water below 20° for not less than 30 mins. The liquid is then diluted with 50 c.c. of 70 per cent. (by volume, S.G. 0·8899) alcohol containing 1 per cent. (by volume) of hydrochloric acid, and placed in water at 17° to 19° for an hour. When the oil contains more than 10 per cent. of arachis oil a precipitate is formed, while pure olive oils give a clear solution (cf. olive oil, p. 272).

The Determination of Arachidic Acid.—The original method for this determination was worked out by Renard (*Compt. Rend.*, 1871, 73, 1330) and depends upon separating the solid acids by means of the lead-salt-ether method and crystallising the arachidic acid from these by means of 90 per cent. alcohol. De Negri and Fabris, Allen and Bellier reported on the process more or less favourably but it was not by any means perfect and it was subjected to a searching, critical examination by Tortelli and Ruggeri (*J.S.C.I.*, 1898, 17, 877). These authors greatly improved the method and their work was confirmed and extended by Archbutt (*J.S.C.I.*, 1898, 17, 1124), whose method is the one chosen for full description here, although Tortelli and Ruggeri maintain that their modification is less cumbersome and leads to more correct results than that of Archbutt.

Archbutt recommends the following modification of Renard's process: Dissolve the fatty acids obtained from 10 grms. of oil (by decomposing the saponified mass with hydrochloric acid under ether and evaporating off the solvent) in 50 c.c. of 90 per cent. alcohol; add to the solution, which must not be allowed to cool below 38° (to prevent separation of crystals), 5 c.c. of a 20 per cent. aqueous solution of lead acetate, cool to about 15°, agitate, allow to stand for half an hour, filter and wash once with ether. Return the soaps into the flask with the aid of ether, digest with ether and repeat this operation three times; lead oleate is thus dissolved out entirely. Transfer the solid soap with the aid of ether into a separating funnel, decompose with hydrochloric acid and wash the ethereal layer until free from mineral acid. Distil off the ether, dry the fatty acids in a water-oven, and pour into the flask 50 c.c. of alcohol of exactly 90 per cent. (spec. grav. 0·8340). Dissolve the fatty acids by warming the (corked) flask, allow to cool to either 15° or 20°, collect the crystals on a small filter and wash three times with 10 c.c. of 90 per cent. alcohol, each time at the same fixed temperature. The filtrate and washings are measured; the necessary corrections are found in the following table :

TABLE CXX.—DETERMINATION OF ARACHIDIC ACID (ARCHBUTT)

For Weights of Fatty Acids obtained by Renard's Process.	Grms. at		
	15°.	17·5°.	20·0°.
0·1 or less	0·033	0·039	0·046
0·2 „	0·048	0·056	0·064
0·3 „	0·055	0·064	0·074
0·4 „	0·061	0·070	0·080
0·5 „	0·064	0·074	0·085
0·6 „	0·067	0·077	0·088
0·7 „	0·069	0·079	0·090
0·8 „	0·070	0·080	0·091
0·9 and upwards	0·071	0·081	0·091

The crystals are thoroughly washed with 70 per cent. alcohol, in which the crude arachidic acid is quite insoluble,* until the washings remain clear on adding water. It is not necessary, although advisable, to redissolve the acids in 50 c.c. of 90 per cent. alcohol and repeat the operation just described. The crystals are dissolved in boiling ether and weighed after drying at 100°. The correction is then added to the weight. The melting-point (capillary tube method) of the mixed arachidic and lignoceric acids so isolated varied from 71 to 72·5°, but even when working in exact accordance with Tortelli and Ruggeri's directions crystals melting at 74–75° could not be obtained by Archbutt, his highest figure being 73·3°. (It may be added that after recrystallising the acids repeatedly from 90 per cent. alcohol the melting-point was raised to 79·6°.)

The above process, although giving excellent results (in fact the proportion of arachis oil present in mixtures can be determined with as great accuracy as that of any other oil), is somewhat lengthy and cumbersome, and this fact led Bellier to attempt a less complicated method which is carried out as follows: Five grms. of the oil are weighed out, saponified with 25 c.c. of alcoholic potash (85 grms. potash dissolved in a litre of 70 per cent. alcohol), and the fatty acids liberated with 7·5 c.c. of dilute acetic acid, which exactly neutralises the potash. The liquid is then cooled rapidly and allowed to stand for an hour to precipitate the fatty acids. After filtering, the fatty acids are washed at 15° to 20° with 70 per cent. alcohol containing 1 per cent. (by volume) of HCl until the filtrate gives no turbidity with water. The precipitate is then dissolved in 25 to 50 c.c. of boiling alcohol of 92 to 93 per cent. strength, and sufficient water added to reduce the strength to 70 per cent. The fatty acids are allowed to crystallise below 20° for an hour, then filtered off, washed with 70 per cent. alcohol until no turbidity is given with water, dissolved in warm ether, crystallised, dried and weighed. Using this method, Bellier obtained 4·2 per cent. of fatty acids from two arachis oils, and none or practically none from several olive oils.

The process has been exhaustively studied by Evers (*Analyst*, 1912, 37, 487) from whose paper many ideas have been taken.

Archbutt (Allen's *Commercial Organic Analysis*, 4th ed., Vol. II, p. 101) states that he has obtained low results by this method.

* Cf. the work of Evers below.

The process was tested by Evers on various oils in conjunction with Renard's process as modified by Archbutt (*ibid.*, p. 93). The results are given in the following table:

TABLE CXXI.—DETERMINATION OF ARACHIDIC ACID (EVERS)

Oil.	RENARD.			BELLIER.		
	Arachidic Acid per cent.	M.Pt. °C.	Arachis Oil per cent.	Arachidic Acid per cent.	M.Pt. °C.	Arachis Oil. per cent.
Arachis (A) . .	4·59	73·5	..	3·56	71	78
Arachis (B) . .	5·15	72·0	..	3·76	71	83
Olive oil, "Nice" Superfine . .	0	..	..	0	..	..
Olive oil "Seconds" .	0	..	..	Trace	..	..
Olive oil Malaga . . .	0	..	..	Trace	..	..
Olive oil, 50% Arachis (A), 50%	2·28	73·5	50	1·36	72	30

The factor used in the calculation of the percentage of arachis oil by Bellier's process is 22, as used by Bellier. It is obvious that the results obtained are exceedingly low. This may be due either to the solubility of arachidic and lignoceric acids in 70 per cent. alcohol, or to the incomplete precipitation of the fatty acids on account of their solubility in the strong solution of oleic and other fatty acids.

Renard (*Compt. Rend.*, 73, 1330) states that these acids are quite insoluble in 70 per cent. alcohol, but the following determinations show that they possess a quite marked solubility:

The acids employed were obtained from arachis oil by Renard's process. The solubility was determined by dissolving about 0·2 grm. of fatty acid in 100 c.c. of 93 per cent. alcohol, adding sufficient water to reduce the strength to 70 per cent., and keeping at a fixed temperature for several hours. The liquid was then filtered at the same temperature, a measured volume of the filtrate evaporated to dryness, and the residue weighed.

The following are mean values of several results obtained by Evers:

Melting-point. °C.	Solubility, Grms. per 100 c.c.	
	At 13°.	At 18°.
71	0·016	0·023
72	0·012	0·017
73	0·009	0·012

The solubility was also determined when the fatty acids were washed on a filter-paper, about 0·2 grm. being used. The results obtained were:

Melting-point. °C.	Grms. dissolved per 100 c.c.
71	0·008
72	0·006
73	0·005

The presence of 1 per cent. of hydrochloric acid in the alcohol does not affect the solubility.

The final modified process of Evers is as follows: Weigh out 5 grms. of the oil into a saponification-flask, add 25 c.c. of alcoholic potash (80 grms. potash dissolved in 80 c.c. water and diluted to a litre with 90 per cent. alcohol) and saponify for about five minutes under a reflux condenser. To the hot soap solution add 7·5 c.c. of acetic acid (1 volume of glacial acetic acid to 2 volumes of water) and 100 c.c. of 70 per cent. alcohol containing 1 per cent. (by volume) of HCl, and cool to 12° to 14° for an hour. Filter and wash with 70 per cent. alcohol containing 1 per cent. HCl at 17° to 19°, the precipitate being broken up occasionally by means of a platinum wire bent into a loop. The washing is continued until the filtrate gives no turbidity with water, the washings being measured. Dissolve the precipitate, according to its bulk, in 25 to 70 c.c. of hot 90 per cent. alcohol, and cool to a fixed temperature between 15° and 20°. If crystals appear in any quantity, allow to stand at this temperature for one to three hours, filter, wash with a measured volume of 90 per cent. alcohol (about half the volume used for crystallisation) and finally with 50 c.c. of 70 per cent. alcohol. Wash the crystals with warm ether into a weighed flask, distil off the ether, dry at 100° and weigh. If the melting-point is lower than 71°, recrystallise from 90 per cent. alcohol. Add the correction for the solubility in 90 per cent. alcohol as in Renard's process, from the table given by Archbutt above and also for the total volume of 70 per cent. alcohol used in precipitating and washing (including the 100 c.c. added in the first instance) from the following table:

TABLE CXXII.—RESULTS FROM EVERS'S FINAL MODIFIED PROCESS

Weight of Acids (corrected for 90 per cent. Alcohol).	Correction per 100 c.c. 70% Alcohol.		
	M.Pt. 71°.	M Pt. 72°.	M.Pt. 73°.
Above 0·10 grm.	0·013 grm.	0·008 grm.	0·006 grm.
„ 0·08–0·10 grm.	0·011 „	0·007 „	0·006 „
„ 0·05–0·08 „	0·009 „	0·007 „	0·005 „
„ 0·02–0·05 „	0·007 „	0·006 „	0·005 „
Less than 0·02 grm.	0·006 „	0·005 „	0·004 „
Factor for conversion of percentage of fatty acids to arachis oil	17	20	22

If there are no crystals from 90 per cent. alcohol, or if they are only in very small amount, add a sufficient quantity of water to reduce the strength

of the alcohol to 70 per cent. (31 c.c. water to 100 c.c. 90 per cent. alcohol). Crystallise at 17°–19° for an hour, filter, wash with 70 per cent. alcohol, and weigh as before, adding the correction for the 70 per cent. alcohol from the above table. If the melting-point is below 71°, recrystallise from a small quantity of 90 per cent. alcohol, or again from 70 per cent. alcohol.

The results obtained by this method are given in the following table:

TABLE CXXIII.—RESULTS FROM EVERS'S FINAL MODIFIED PROCESS

Oil.	Alcohol used for Crystallisation. Per cent.	Weight of Crystals.	Correction for 90 per cent. Alcohol.	Correction for 70 per cent. Alcohol.	Total.	Per cent.	M.Pt. °C.	Per cent. of Arachis Oil by Factor
		Grm.	Grm.	Grm.	Grm.			
Arachis (A)	90	0·160	0·040	0·027	0·227	4·54	73	100
	70	0·218	..	0·065	0·283	5·66	71	96
Arachis (B)	90	0·163	0·045	0·032	0·240	4·80	72	96
	70	0·233	..	0·068	0·301	6·02	71	102
Arachis (C)	90	0·152	0·054	0·034	0·240	4·80	72	96
Arachis (D)	90	0·194	0·033	0·028	0·255	5·10	72	102
Arachis (A), 50%	90	0·056	0·032	0·022	0·110	2·20	73	48
Olive "Nice," 50%	70	0·090	..	0·055	0·145	2·90	71	49
Arachis (A), 35%	90	0·045	0·020	0·029	0·094	1·88	71	32
Olive "Nice," 65%	90	0·029	0·040	0·020	0·089	1·78	72·5	37
	70	0·059	..	0·040	0·099	1·98	71	34
Arachis (A), 20%	90	0·024	0·012	0·019	0·055	1·10	71	19
Olive "Nice," 80%	70	0·030	..	0·024	0·054	1·08	71	18
Arachis (C), 20%	90	0·012	0·020	0·015	0·047	0·94	72	19
Olive "Malaga," 80%	70	0·021	..	0·027	0·048	0·96	71	16
Arachis (A), 10%	90	0·009	0·008	0·008	0·025	0·050	73	11
Olive "Nice," 90%	70	0·008	..	0·015†	0·023	0·046	70	8
Arachis (B), 10%	90	0	..	..	..	0	..	..
Olive "Nice," 90%	70	0·012	..	0·018	0·030	0·60	71	10
Arachis (C), 10%	90	0	..	..	..	0	..	..
Olive "Malaga," 90%	70	0·011	..	0·016	0·027	0·54	71	9
Arachis (A), 5%								
Olive "Nice," 95%	70	0·007	..	0·012†	0·019	0·38	..	6·5
Sesamé	90	0	..	..	..	0	..	..
	70	0·012	..	..	..	0·24	64	..
Cotton-seed	90	0	..	..	..	0	..	..
	70	0·006	..	..	..	0·12	50–55	..
Olive "saponified"	90	0·014	..	..	..	0·28	64–67	..
	70	0·021	..	..	..	0·42	64–68	..

Various other methods for the separation of arachidic acid have been proposed in recent years. Fachini and Dorta have worked out a method depending upon the solubility of the potassium salts in acetone (*Analyst*,

* This result was obtained by recrystallising the fatty acids obtained from 70 per cent. alcohol from 10 c.c. of 90 per cent. alcohol.

† In these cases the correction has been added for melting-point 71°.

1914, 39, 122) which has been recommended by Pritzker and Jurgkunz (*Analyst*, 1922, 47, 124) although Rideal and Acland (*Analyst*, 1913, 38, 260) have described the method as practically useless. Kerr (*Analyst*, 1916, 41, 381) recommends a method which depends upon the solubility of the magnesium salts in ether, a similar process being described by Thomas and Yu (*Analyst*, 1923, 48, 126). These and similar methods have no obvious advantages over the modified Bellier method described above, so that readers must be referred to the abstracts or the original papers for the full details involved. It may be that a more expeditious method can be devised, but at the moment these new methods have not yet received the extended trial which is advisable. It would be a useful piece of work for these new methods to be compared with the Evers modification of the Bellier process.

Hydrogenated Arachis Oil.—Arachis oil may be converted into a hard white fat by catalytic hydrogenation. The oleic and linolic acids are reduced to stearic acid, and in the case of an oil of iodine value 82·5 Myddleton and Barry have shown that (*Fats: Natural and Synthetic*, London 1924) when the iodine value had been reduced to 25·9 by this method the stearic acid had increased from 6·0 to 32·6 per cent., whilst that of oleic had been reduced from 51·6 to 23·0, and that of linolic from 26·0 to 0·0. Heim, Job and Struzwage (*J.S.C.I.*, 1919, 38, 426A) hydrogenated the oil with nickel formate as catalyst and produced a product which had M.Pt. 58°, Sol. Pt. 47·8° and iodine value 13·5. Mailhe (*J.S.C.I.*, 1922, 41, 598A) passed the oil over an aluminium copper catalyst at 600°, freed the product from acids and then passed it over nickel at 180°–200° when he found methane and benzene hydrocarbons to be formed. The qualitative test for arachis oil will fail, but the quantitative methods for its determination, as has been shown by Kreis and Roth (*J.S.C.I.*, 1913, 32, 201), are still available.

Examination for Adulteration.—Although arachis oil has been largely used to adulterate olive oil it is itself liable to adulteration with other seed oils which happen to be cheaper at the moment. In the past sesamé, cotton-seed, poppy-seed, rape, have been used for this purpose and the reoccurrence of the use of these and similar oils for this purpose is not unlikely.

The specification for the best edible arachis oil in the United States of America as defined by the Interstate Crushers' Association is as follows: " Choice pea-nut oil must be sweet in odour and flavour, prime in colour, clear and brilliant in appearance and free from moisture, and shall not contain more than one-tenth per cent. of free fatty acid. Prime yellow pea-nut oil must be clear, sweet in odour and flavour, free from water and settlings, and of no deeper colour than fifty yellow and five red on Lovibond's equivalent colour scale."

The addition of any quantity of other seed oil will appreciably lower the amount of arachidic acid obtained in the Evers method. The amount so obtained varies from 4·5–5·3, and any oil giving less than 4·3 per cent. of arachidic acid (crystallised from 90 per cent. alcohol) should be looked upon with grave suspicion. The iodine value should be about 90. Although genuine samples have been reported with iodine values of 100 or more these are distinctly on the high side and the figure is not usually over 95. The saponification value should not be less than 190. The titre value should be about 29°, whilst the solidifying point of the oil is about 3° to 0·0°, one observer states that the oil becomes turbid at 3°, congeals at −3° and becomes solid at −7°. Colour tests for sesamé and cotton-seed oils may be carried out, but it should be remembered that arachis oil is frequently pressed in the same presses as sesamé oil and that, therefore, commercial samples of the

former may give a faint reaction for sesamé oil.* A very faint reaction may, therefore, be disregarded and a strong one should be carefully confirmed by means of the iodine value, titre test and the arachidic acid content. The poorer classes of Porto Rico are said to use the oil flavoured with nitrobenzene (Lucas, *Analyst*, 1913, 38, 457). The nitrobenzene may be determined by shaking the oil with zinc dust and hydrochloric acid and removing the aniline hydrochloride by washing out with water. Dekker (*Analyst*, 1923, 48, 126) has described an oil from the seeds of *Hibiscus cannabinus* which closely resembles arachis oil.

" Arachis butter " is a preparation prepared by natives from the slightly roasted kernels of the nuts. Utt (*Analyst*, 1914, 39, 481) found 23 commercial samples to contain 44·74–53·64 per cent. of fat which had an index of refraction at 40° of 1·4630–1·4653 and iodine values of 88·04–94·36. Three samples prepared in the laboratory contained 50·65–52·03 per cent. of oil with index of refraction at 40°, 1·4631 and iodine value 88·75–90·03.

* Sesamé oil used to be found in the crude oils from India and China, due probably to carelessness rather than deliberate adulteration.

CHAPTER XIX

OLIVE OIL

Olive oil is obtained from the fruit of the tree *Olea europœa* (var. *sativa*), L.

"At what remote period of human progress the wild *oleaster* passed under the care of the husbandman and became the fruitful garden olive it is impossible to conjecture. It is frequently referred to in the Bible and Homer's *Iliad*, and all tradition points to the limestone hills of Attica as the seat of its first cultivation in Greece. By Solon's time it had increased to such an extent that laws were framed to regulate its cultivation, and Pliny refers to it as growing abundantly in Spain and the two Gallic provinces. In Egypt it did not flourish, and the olive oil found in the Theban tombs was probably imported from Syria. Along the southern shores of the great Mediterranean the tree was carried by the Phœnicians, at a remote period, to their numerous colonies in Africa, to southern Spain and Sardinia, and perhaps also to the Canary Islands. Yielding a grateful substitute for the butter and animal fats consumed by the races of the north, the olive, in the south, became an emblem not only of peace but of national wealth and domestic plenty; and of victory, too, forming the crown alike of the Olympic victor and the Roman conqueror. Among the Greeks and Romans the oil was valued as an article of diet as well as for external use. The unripe fruit, steeped in brine, was much valued, and pickled olives have been found among the buried stores of Pompeii. The bitter juice deposited during expression of the oil (called *Amurca*, whence Marc is derived) and the astringent leaves of the tree have many virtues attributed to them by ancient writers." (*Chemical Age*, 1923, 8, 453.)

At the present time the olive tree is cultivated in nearly all the countries bordering on the Mediterranean, and in later years cultivation has extended to Australia, California and South Africa. The yield of oil from the fruits grown in non-European countries is considerably inferior to that from the Mediterranean olives and, although considerable efforts have been made by the U.S. Dept. of Agriculture to effect improvement, and some improvement has been the result, yet much remains to be done.

The tree is subject to various diseases, thus fungi attack the shoots, whilst the olive fly, *Mosca olivarum* (*mouche de l'olive*) attacks the fruits with deadly effect and great care and attention are necessary to protect the orchards from these and other pests.

A large number of various grades of oil are known in commerce. The finest qualities (known as virgin oil) are produced by hand-picking the fruits, selecting those that are only just ripe, peeling them and hand-pressing in cloths. The oil is treated with water and allowed to stand—when perfectly bright the oil is skimmed off.

The best ordinary grades are prepared by crushing the nearly ripe fruits without breaking the kernels and grinding the mass to a pulp. The pulp is then pressed in hydraulic presses in the cold. For lower-grade oils cold water is then added to the marc and pressure again applied after which the process is repeated using hot water in place of cold. The press cake still contains considerable quantities of oil in some cases up to 20 per cent. and even more. This is removed by extraction. Previously carbon bisulphide

was used for this purpose almost exclusively (producing the " sulphur olive oils ") but more recently ethylene trichloride has been used on account of the much reduced possibility of fire. (Cf. *Chemical Age*, 1923, 8, 452.)

In some cases the marcs from the earlier pressings are thrown into pits where fermentation sets in, after which the whole mass is ground to crush the stones, mixed with boiling water, and strongly pressed (*huile d'enfer*). The press cake is then extracted as before. The oils known as olive residuum oils (*huiles des grignons d'olives*), are frequently washed with alkali and then with water and are allowed to settle. They are frequently known as neutral or " saponified " oils. They are characterised by turbidity, due partly to traces of water, and by a high proportion of unsaponifiable matter. See page 272. The liquid taken from the pits where the marc ferments, and other aqueous fluids obtained during the production of olive oil, are rich in potash and nitrogenous substances, but up to the present they have not been utilised. (Cf. Chevalier, *J.S.C.I.*, 1916, 35, 1120; Cruess and Christie, *ibid.*, 1917, 36, 147.) For the production of neutral pharmaceutical oils see Cordier and Lesure (*ibid.*, 1917, 36, 722).

In a French consular report (*J.S.C.I.*, 1911, 30, 1071) it was stated that Italian producers decolourised with citric acid or tannin, usually the latter. The amount of tannin varies between 1 and 5 per cent. according to the colour of the original oil and the degree of bleaching desired. Another method which was described as a " safe " one was to allow the oil to fall as a fine sprey from a height of about six metres into a large vessel partly filled with water and so arranged that the oil is exposed to air and sunlight. Klein (*J.S.C.I.*, 1912, 31, 593) is of opinion that only fresh olives and those pickled in brine can yield a good pale edible oil, others giving oils which are too dark and which have a too high acid value.

Ventre has a useful paper on the preparation of olive oil of which the following is an abstract (*J.S.C.I.*, 1915, 34, 236): " He states that the increased yield of oil due to late harvesting of olives is only apparent, being due to the loss of water by evaporation. The best time for plucking is when the skin is red or black, and without wrinkles; if delayed too long, the yield of oil is diminished. The proportion of oil to dry matter is not sensibly affected by storage, provided ventilation is adequate and the olives are placed in layers not exceeding 16 inches in depth. The quality of the fruit is not diminished by storage for a certain time, and the yield of oil may be increased. Heated olives give a better yield of oil; the optimum temperature (35–40°.) should be obtained by natural fermentation. A comparison of the relative efficiency of hydraulic and mechanical presses showed that the former have a slight advantage, and should, therefore, be employed in large factories. The addition of water gives a better extraction, but hot water is no better than cold."

Degli Atti (*J.S.C.I.*, 1915, 34, 288) states that when the maceration of olive pulp is prolonged unduly, oil is obtained which, although of good quality, is strongly coloured. The best method for the decolourisation of such oils is treatment with 5 per cent. of finely powdered animal charcoal for seven days. Artmann (*J.S.C.I.*, 1920, 39, 120A) has shown that the colour of the oils seems to be due to three different pigments respectively, yellow, green and brown, and that some filtering agents show a selective absorption for one of these. Mastbaum (*J.S.C.I.*, 1922, 41, 674A) has given an account of current methods of pressing in Spain, many of which he describes as being crude; he makes several valuable suggestions for the improvement of the Spanish industry.

Ripe olives have been known to contain as much as 70 per cent. of oil

but this figure is exceptional, the freshly-prepared olives of the best cultivated varieties containing from 40–60 per cent. Algerian olives may contain as low a proportion of oil as 10 per cent., whilst rarely rising to more than 35 per cent., whilst Tunisian olives contain from 20 to 50 per cent. of oil. Corsican olives contain 25–37 per cent. of oil (P. Sajous, *J.S.C.I.*, 1924, 43, B1018). The amount of oil contained in the olives cultivated in recent years in California is low, an oil content of 30 per cent. has not yet been reached whilst figures of less than 20 are very common. The acidity of the oil in olives is dealt with by R. Marcille (*Analyst*, 1925, 50, 27).

Composition.—Olive oil contains a large proportion of oleic acid and a quantity of solid acids which have been variously estimated as from 2 per cent. to 25 per cent., but how much of this variation is due to faulty methods of examination and how much to real differences in composition of oils from various sources can scarcely be said to be yet definitely decided. Tunisian oils from Sfax contain, according to Bertainchand, up to 25 per cent. of solid fatty acids, such oils would, of course, have a portion of the " stearine " removed before being placed on the market.

The solid fatty acids consist largely of palmitic acid. A trace of arachidic acid has been reported by some workers and is probably present but the quantity is so small that no deposit is obtained in any of the ordinary methods for the determination of this acid in oils. Hehner and Mitchell (*Analyst*, 1896, 21, 328) failed to obtain crystals of stearic acid from olive oil by their well-known method and on the strength of this Lewkowitsch states that the absence of stearin must be taken as proven. It must be remembered, however, that the same test fails to reveal more than a mere trace of stearic acid in butter fat, which fat has been shown by other methods to contain considerable quantities, so that the absence of stearic acid requires further investigation.

The liquid fatty acids contain a large proportion of oleic acid, but it seems to have been proved beyond reasonable doubt that a proportion of linolic acid is also present. The relative proportions of oleic acid to linolic acid varies in different samples of oil but the quantity of linolic is about one-tenth (or somewhat less) that of the oleic. Myddleton and Barry (*Fats: Natural and Synthetic*, page 107) give the composition of the acids as palmitic, 14·6 per cent.; oleic, 75·4 per cent.; and linolic, 10·0 per cent.

Jamieson and Baughman (*J.O.F.I.*, 1925, 2, 40) have examined the composition of Californian olive oil. They found that this oil consists of the glycerides of oleic acid, 84·6; linolic acid, 4·6; myristic acid a trace; palmitic acid, 6·7; stearic acid, 2·3; arachidic acid, 0·1; and unsaponifiable matter, 1·0. Lapworth and Mottram (*J.S.C.*, 1925, 127, 1628) give oleic acid, 72; linolic, 12–13; higher saturated acids, 14–15; and unsaponifiable matter, 1·4 per cent.

Properties.—Olive oil has been well described as the edible oil *par excellence*. The taste of the best varieties is bland and pleasant and their appearance clear and bright. A small amount of stearine is deposited in the case of fresh oils on cooling to temperatures below 15°, especially in the case of oils from certain districts which contain a considerable amount of " stearine," but when this has once been removed by cooling and decantation the oil will remain clear and bright for long periods. The oil is a non-drying oil which does not easily turn rancid when it has been removed from the marc. In the Livache test an absorption of about 1 is obtained, compared with about 15 for linseed oil. The high acidity and rancidity of many of the cheaper varieties of oil are due to the fact that they have been allowed to remain with the marc after the earlier extractions, or that they have been produced

TABLE CXXIV.—CHARACTERISTICS OF OLIVE OIL

Authority.	S.G. 15°.	Sap. Value.	R.I. 40°.	Wijs.	Unsap. per cent.	Free Acid per cent.	Titre.	R.M.	Sol. Pt.
B.P.	0·915 0·918	188–197	1·4605 1·4635	79–87	..	Not more than 6·0	..	..	..
Southall's Annual Reports	0·914– 0·918	185·3– 196·8	1·4619– 1·4627	77·6– 87·9	..	Not more than 1 per cent.*	..	..	..
Evan's Annual Reports	0·915– 0·918	185–197	1·4609– 1·4625	79·0– 90·5	..	..	..	..	..
Fryer and Weston	0·915 0·918	190–195	1·4623– 1·4635	80–85	0·5– 2·0	0·5–2·0 for edible	18–22	..	..
Leach	0·916– 0·918	185–196	1·4621	79–88	0·5– 1·0	..	17–26	0·6	–6 to ?
U.S.P.	0·910– 0·915	190–195	..	79–90	..	..	..	..	..
Thomson and Dunlop, *Analyst*, 1906, 31, 282	0·9144– 0·9159	190·7– 195·6	1·4602– 1·4618	81·2– 89·1	1·24– 1·62	..	..	..	..
Archbutt, *J.S.C.I.*, 1907, 26, 453, 1185	0·9162– 0·9178	189·0– 191·9	..	82·4–† 91·1	0·72– 1·15	0·77– 1·15	..	Algerian and Tunisian	
Marcille, *Analyst*, 1907, 32, 257; 1910, 35, 479	..	..	..	81·2–‡ 84·5	..	..	..	I.V. liquid fatty acids. 104–108.	
Portuguese standard, *Analyst*, 1911, 36, 502	0·918 0·918	182–202	1·4605– 1·4615	75–85	..	Not more than 1·6	..	..	2–4
Klein, *J.S.C.I.*, 1912, 31, 593	0·915– 0·918	185–195	1·4608– 1·4628	75–85	..	..	..	Portuguese oils	
Villavecchia	0·914– 0·919	(185–196) 192–195	1·4617– 1·6424	80–83 (79–88)	..	Not more than 2 for edible	21–24	0·3	0–6

* Not more than 4 per cent. for pharmaceutical purposes.

† One sample had 94·7.

‡ Tunisian, 87·9–92·5.

from over-ripe seeds. The property of the oil varies to a considerable extent depending upon the variety of tree, the degree of ripeness of the fruit, the method of gathering and the method used to obtain the oil. The taste of some oils is harsh and bitter as, for instance, the Puglia olive oils, but this harshness disappears on keeping. The harsher oils such as Tunisian are frequently mixed with better quality oils so that the objectionable flavour will be less noticeable. Canzoneri and Bianchini (*Analyst*, 1914, 39, 255) consider that rancidity in olive oil is caused by oxidation promoted by light. For the solubility of olive oil in alcohol see Fachini and Somazzi (*J.S.C.I.*, 1925, 44, B250).

Tests for Adulteration.—There are no special tests which may be applied for the detection of olive oil in mixtures and also no single test which, applied to the oil, will decide whether it is genuine or otherwise. An opinion on the purity of an oil must be given on a general consideration of the analytical characters of the oil together with the indications produced by the application of specific tests for various likely adulterants. The most important single determination is that of the iodine value. In genuine oils this usually lies between 81 and 85, but an oil having a value outside these is not necessarily adulterated as some Tunisian olive oils of undoubted purity have given iodine values as high as 94·7, whilst a Mogador oil (Thomson and Dunlop, *Analyst*, 1906, 31, 282), which had refractive index at 40° of 1·4608, saponification value 190·7, S.G., 0·9150 and 24·72 of free oleic acid, had an iodine value of 94·3. In spite of these high iodine values which have been obtained from genuine oils any oil which gives an iodine value approaching 90 must be looked upon with suspicion, and should be very carefully examined for possible adulterants. The iodine values of most of the probable adulterants are much higher than olive oil with certain notable exceptions such as arachis oil, for which latter there is, fortunately, a specific test. On account of these fluctuations the use of colour reactions is preferred by J. Sonol (*J.S.C.I.*, 1925, 44, B16).

Tolman and Munson (*Bull. No.* 77, U.S. Dept. of Agriculture) give a large number of analyses of genuine Californian olive oils obtained from all parts of the State and representing the different soils and climatic conditions. The iodine values of 42 samples ranged from 78·5 to 89·8, with an average of 85·1. Eleven samples examined by Blasdale ranged from 80·0 to 86·5; average 84·0. Samples of known purity examined by Colby ranged from 77·7 to 93·5. Tolman and Munson have found that the iodine value increases as the percentage of solid fatty acids and the M.Pt. of the mixed fatty acids decrease, and they recommend that the iodine value should be considered in conjunction with these other factors and with the iodine value of the liquid fatty acids. They give the following table:

TABLE CXXV.—RELATION BETWEEN IODINE VALUE, SOLID FATTY ACIDS AND M.PT. OF MIXED FATTY ACIDS (CALIFORNIA OILS)

Iodine Value.	Solid Fatty Acids per cent.	M.Pt. of Mixed Fatty Acids.	Iodine Value.	Solid Fatty Acids per cent.	M.Pt. of Mixed Fatty Acids.
79·9	10·91	31·0	85·6	4·92	21·3
83·0	7·62	28·0	85·7	6·27	23·4
82·9	5·70	25·0	86·2	3·39	21·1
84·3	7·23	23·4	88·2	4·42	23·5
85·6	5·12	22·6	88·5	2·43	20·2

The oils which have been used to adulterate or substitute olive oil have included arachis, rape, cotton-seed, sesamé, soya-bean, poppy-seed, maize oil, sunflower oil, lard oil and mineral oil. (Cf. Sejen-nut oil, page 247). Some suggestions for detecting these oils will be given below under the heading of each oil.

The high iodine values of certain Moroccan oils has been ascribed by Sassarath to the use of the oil of *Arganum sideroxylon* for which see page 244.

Arachis Oil may be detected by the qualitative test given under arachis oil on page 260. A negative result by this test is definite proof of the absence of arachis oil, but a positive test is not conclusive proof of its presence. Thus Archbutt (*J.S.C.I.*, 1898, 17, 1009) has found arachidic acid in rape and mustard oils so that a trace might be due to the presence of either of these. The same worker has also shown (*ibid.*, 1911, 30, 5) that certain olive residuum oils (known as " neutral " or " saponified " oils) give a slight reaction with the qualitative test; tomato-seed oil is also stated to contain notable quantities of arachidic acid. In every case where a slight positive reaction occurs in the qualitative test which is not due to arachidic acid (and therefore not due to the presence of a foreign oil) no residue will be obtained in the quantitative test when carried out as described on page 260. Lüers (*J.C.S.*, 1913, 104, ii, 163) considers that this precipitate is due in certain cases, where the oil contains much myristin, to the formation of an acid potassium salt of myristic acid and states that the precipitate can be avoided by adding three drops of glacial acetic acid (in addition to the prescribed amount) to the saponified oil.

To avoid any difficulty A. D. Powell (*Analyst*, 1925, 50, 395. Cf. Shelley, *ibid.*, p. 498) suggests the following modification of the test:

> One grm. of olive oil is saponified with 5 c.c. of 2N alcoholic potassium hydroxide solution (made with 90 per cent. alcohol), the mixture being treated under a reflux condenser for 5 minutes. After dilution with 25 c.c. of water, the solution is well shaken with 30 c.c. of ether to remove the greater portion of the unsaponifiable matter; the separated aqueous solution is acidified with 2 c.c. of concentrated hydrochloric acid, and the fatty acids extracted by shaking with 20 c.c. of ether. This ethereal solution, after being washed once with 10 c.c. of water, is evaporated, and the fatty acids heated in the water-oven for about 10 minutes. The separated fatty acids are dissolved in 50 c.c. of 70 per cent. alcohol, and the solution cooled to 14° to 15° C., and maintained at that temperature for an hour, or longer if necessary. In the greater proportion of oils tested 5 per cent. of arachis oil caused a precipitate at 15° C. in about half an hour, but in the case of an oil containing a high proportion of liquid fatty acids, cooling to 14° C., may be necessary to induce precipitation. Most oils which are free from arachis oil remain clear at 12° C.; in exceptional cases a precipitate may occur at 14° to 15° C. The melting-point of the precipitate should, therefore, be taken in all cases where precipitation occurs above 14° C.
>
> In the absence of arachidic acid, the original precipitate, after being well washed with cold 70 per cent. alcohol to remove soluble fatty acids, melts at about 52° to 54° C., and, after recrystallisation from 90 per cent. alcohol, at about 60°–61° C. The precipitate from oils containing from 5 to 10 per cent. of arachis oil melts between 60° and 65° C., and one recrystallisation from 90 per cent. alcohol is usually sufficient to raise the melting-point above 70° C.

Cf. Biazzo and Vigdoreik (*Analyst*, 1917, 42, 85); Lund (*J.S.C.I.*, 1917, 36, 722). Pecan-nut oil, page 209, Queensland nut-oil, page 245. For a colour test see Sisley and Frehse (*Analyst*, 1914, 39, 228). Cf. also Frehse (*J.S.C.I.*, 1925, 44, B512).

Rape Oil when present will tend to lower the saponification value and increase the iodine value. The characteristic acid of rape oil, erucic acid, may be detected by the method of Tortelli and Fortini which is fully described on page 228. Kreis (*Analyst*, 1913, 38, 434) has suggested the following method for the detection of rape oil: The fatty acids from 20 grms. of the oil are dissolved in 100 c.c. of 95 per cent. alcohol, and the boiling solution is treated with 1·5 grm. of lead acetate dissolved in 50 c.c. of alcohol. After standing for twelve hours at a temperature below 15°, the lead salts are collected, washed three times with alcohol, and the fatty acids are liberated from the salts by treatment with hydrochloric acid. The fatty acids thus obtained are again dissolved in 100 c.c. of alcohol, and the boiling solution is treated with 1 grm. of lead acetate dissolved in 50 c.c. of alcohol. After twelve hours the lead salts are separated by filtration, and the fatty acids remaining in the filtrate are recovered by evaporating off the alcohol and treating the residue with dilute hydrochloric acid. The melting-point of this fraction of the fatty acids is now determined. In the case of pure olive oil it will be about 47° C., but is considerably lower when rape oil is present. He claims that the method will detect the presence of as little as 5 per cent. of rape oil in olive oil. Biazzo and Vigdorcik (*Analyst*, 1917, 42, 86) base a method of detection on the potassium-salt-acetone method and reduction of the erucic acid to behenic acid.

Cotton-Seed Oil in any quantity will cause an increase in the iodine value and the specific gravity. An olive oil having a specific gravity of more than 0·918 (particularly if it is pale; the darker oils, are, as a rule, somewhat higher in gravity and have been known to have S.G. as high as 0·920) needs careful consideration before it is passed as genuine. The Halphen test for cotton-seed oil should be applied. Occasionally genuine olive oils give a slight reaction with this test (cf. Sage, *J.S.C.I.*, 1915, 34, 184; Prax, *ibid.*, 1921, 40, 778A), and at other times an oil containing cotton-seed oil fails to give the reaction. It has, however, been stated (*Southall's Annual Reports*, 1911, 13) that cotton-seed oil may sometimes be detected by means of the nitric acid test (shaking with an equal volume of nitric acid of S.G. 1·375) when the Halphen gives no reaction.

Sesamé Oil, like the other semi-drying oils, will increase the specific gravity and the iodine value. It may be specifically recognised by means of the Baudouin reaction. Some olive oils, particularly those from Tunis, give slight reactions with the Baudouin reagent although quite free from sesamé oil—very slight indications may therefore usually be disregarded with perfect safety. Sage (*J.S.C.I.*, 1915, 34, 184) states that such oils give a characteristic change of colour with the Villavecchia modification of the Baudouin test. With this test the abnormal oils give a pink colour changing to lilac in one hour, whilst in the case of those actually containing sesamé oil the original pink colour persists for this length of time. Marcille (*Analyst*, 1910, 35, 479) states that the substance in Tunis oil giving the Baudouin reaction may be removed by washing the oil with a dilute solution of sodium carbonate. Prax (*J.C.S.*, 1922, 122, ii, 595) states that the colouring matter can be removed by shaking the oil with its own volume of 90 per cent. alcohol containing 10 per cent. of ammonia and evaporating off the alcohol and ammonia on the water-bath before applying the test.

Lard Oil has been used at times as an adulterant. The odour of the oil, especially on warming, will be some guide in this case and Lewkowitsch suggests that the viscosity and the melting-point of the fatty acids may also be of some use. Lard oil has M.Pt. of fatty acids about 35° and titre test about 31°, whilst olive oil has 22°–28° for the former and 21°–24° for the latter. Where, however, lard oil or other animal oil is suspected the phytosteryl acetate test should be carried out. The phytosterol of olive oil has M.Pt. 135°–136·5°, whilst the acetate has M.Pt. 120°–121°.

Mineral Oils and unsaponifiable matter will be shown by a lowering of the saponification value and an increase in the amount of unsaponifiable matter. The neutralised alcoholic solution obtained after the determination of the saponification value should remain clear and bright on the addition of twice its volume of water.

Other Vegetable Oils which are likely to be used will usually be indicated by taste—a most important test, but one requiring care and experience—and the increase in the iodine value. In addition to the oils mentioned above some other oils, which closely resemble olive oils, may be used as adulterants or substitutes. These are cornel oil, calumpang-nut oil (Java olive oil), caskew-kernel oil, and tea-seed oil. The detection of these oils is difficult—the suggestions that have been made will be found under the head of these oils on pages 237–248.

Other Methods of Examination.—The Maumené test and the elaidin test are quite characteristic of olive oil, and Archbutt (*J.S.C.I.*, 1886, 5, 303) has given figures which tend to show that an admixture of 10 per cent. of rape or cotton-seed oil would be detected by the latter test, but such an admixture could be detected with equal certainty (or uncertainty) by other tests, so that, in general, it will not be necessary to apply this test. The figures given by olive oil in the Maumené test are lower than those of most other vegetable oils, but the indications given are of no greater value than those of other tests. Mazzaron has suggested a novel test (*Analyst*, 1916, 41, 135) by which the volume of sulphur dioxide generated during the carrying out of the Maumené test is measured. The sulphur dioxide value is defined by this author as the number of c.c. of N/10 iodine solution required by the sulphur dioxide evolved when 20 c.c. of oil are treated with 5 c.c. of pure sulphuric acid. This value varies in the case of olive oil from 2·1–2·6, whilst in the case of sesamé it is 49½; cotton-seed, 137½; soya-bean, 223. Maize oil has a sulphur dioxide value of 65, whilst those of colza and arachis oils are 15 and 7 respectively.

This method has been examined by Morton and Spencer (*J.O.F.I.*, 1924, 1, 66), who propose the following apparatus: The apparatus consists of a Pyrex test-tube, 10 by 1½ inches. The rounded bottom of this tube must be as nearly hemispherical as possible. A glass stirring paddle, the blades of which are 3 cm. from tip to tip and 1 cm. deep, is provided. The blades conform in shape to the rounded bottom of the tube and are turned to give, as nearly as possible, an upward movement to the liquid. A three-hole rubber stopper closes the tube, the centre hole being large enough to admit a mercury seal, the other two holes carrying glass tubes of 4 mm. inside diameter. The shaft of the glass paddle passes through the mercury seal and is attached to the shaft of a stirring motor regulated to run at 300 r. p.m. The absorption end of the apparatus consists of three 200 c.c. Erlenmeyer flasks each provided with a two-hole rubber stopper and glass connecting tubes. Glass tubing of 4 mm. inside diameter is used throughout.

The reaction is conducted in a constant temperature bath maintained at 25·5° to 26°. This bath can readily be constructed from an empty

ether can. A $\frac{3}{8}$ inch overflow is provided about an inch from the rim.

Running tap-water is passed into the can through a quarter-inch copper coil heated with a Bunsen flame, and the temperature of the bath is controlled by the rate of flow of the water and the heat applied. The authors have found this to be a very efficient and convenient means of bath control, the variation not exceeding 0·5°. It has the advantage of being portable and easily manipulated. The test-tube can be so adjusted that tilting alone is sufficient to remove the bath without disturbing the apparatus above it. The overflow of the bath can serve as an additional bath in which the sulphuric acid and oil under examination may be brought to a uniform and constant temperature before making the determination.

The actual determination is carried out as follows:

" Sulphuric acid (98·5 per cent.) prepared by boiling the ordinary 95 per cent. acid in an open casserole to about two-thirds of its original volume. It is poured hot into a Pyrex-Erlenmeyer flask and cooled under a calcium chloride tube. This acid must be carefully made to a uniform and definite strength and kept well protected.

" 2. Iodine, tenth-normal solution.
" 3. Sodium thiosulphate, tenth-normal solution.
" 4. Starch, 0·5 per cent. solution.
" 5. Mercury."

Determination

Measure into the first 200 c.c. Erlenmeyer flask enough tenth-normal iodine solution to assure an excess of about 15 c.c. and bring the volume to about 150 c.c. with water. To the second flask add 5 c.c. of the tenth-normal iodine solution and bring the volume to about 150 c.c. To the third flask add 1 grm. of potassium iodide and 2 c.c. of starch solution and dilute to about 100 c.c. Connect the three flasks and aspirate through the apparatus and regulate the rate to about 180 bubbles a minute.

Bring the sample of oil and the sulphuric acid to 25·5 to 26° in the constant temperature bath. Measure with a pipette 20 c.c. of the oil and introduce it into the digestion chamber by placing the tip of the pipette near the bottom and touching the side of the tube. Be sure that no oil touches the side of the tube above the level that will be reached when the sulphuric acid is added. Allow the pipette to drain for 10 minutes. Carefully pipette 5 c.c. of the sulphuric acid into the test-tube by placing the tip of the pipette just above the level of the oil, touching the side of the tube, and allow the acid to underlie the oil with as little disturbance as possible. All premature mixing must be avoided. Connect the test-tube with the stirring apparatus but do not let the paddle dip into the mixture. Place the constant temperature bath directly under the test-tube. Raise the test-tube to its proper position and fasten in place. Make the connection to the absorption flasks. Elevate the constant temperature bath to submerge about 6 inches of the test-tube. Disconnect the aspirating tube. Place a finger over the open end of the intake tube and start the stirrer. Steady the digestion tube with the hand to eliminate friction as much as possible. When the reaction subsides, as indicated by the backing up of the solution in the first flask release the finger from the intake tube, reattach the aspirating tube and continue the aspiration at the predetermined rate. Stir for exactly 10 minutes. At the end of 30 minutes disconnect the absorption flasks and titrate the excess of iodine with tenth-normal thiosulphate. The

number of cubic centimetres of tenth-normal iodine consumed is the sulphuric index of the oil.

By this method these observers obtained the following results:

TABLE CXXVI.—SULPHURIC INDEX OF VARIOUS OILS

Oil.	Sulphuric Index.	Iodine Value.
Olive, California . .	2·1	..
	2·54	..
	2·60	..
	2·2	81·3
Italian	1·00	82·2
	1·21	80·0
Tea-seed	1·62	83·0
Coconut	0·80	6·9
Sesamé	52·67	..
	51·97	109·1
Apricot	15·1	..
	14·3	107·1
Peanut, cold pressed .	5·73	97·1
Sunflower seed . . .	138·1	130·8
Cotton-seed	53·8–92·7	102·0–112·2

Morton and Spencer observe that the sulphuric index has a place in the record of analysis of cotton-seed oil. The conditions entering into this determination can be controlled, but if the results are to have any value the method must be followed with care and expert manipulation. As a routine method it does not compare with that for the iodine number in the number of determinations that can be made in a given time, but as a means of identification of an unadulterated oil it compares favourably. The extent of adulteration of cotton-seed oil with olive oil may be determined within a definite limit, but the reverse is not true. A large proportion of cotton-seed oil can be added to olive oil, without increasing the index measurably.

Extracted Olive Oils are not legitimately sold for edible purposes, for which they are quite unsuitable. The extraction is frequently carried out with carbon bisulphide so that traces of this solvent and other organic sulphur compounds are usually found in the oils, moreover as the extraction is always carried out on the press cake, frequently after this has been allowed to ferment, very high percentages of fatty acids are usually present and amounts up to 70 per cent. have been recorded.

Canzoneri and Bianchini (*J.S.C.I.*, 1914, 33, 1017) examined six extracted oils at length and found S.G. 0·9168–0·9198; R.I. at 40°, 1·4598–1·4627; iodine value 74·1–77·9; titre, 17·5°–19·7°; acidity, 2·65–55·9 per cent. as oleic; ash, 0·046–0·056 per cent. Total sulphur, as $BaSO_4$, 0·4–0·55 per cent., acetyl value, 31. They recommend that carbon bisulphide be detected by distilling with steam and testing the first portion of the distillate with a dilute solution of copper sulphate, or with amyl alcohol and kapok oil (or cotton-seed oil) as in the Halphen test. Stadlinger (*ibid.*, 1920, 39, 663A) tested forty-seven samples of extracted oils and found the unsaponifiable

matter to vary from 0·2–9·6 per cent., and the oxidised fatty acids from 1·3–12·8 per cent. He states that for the determination of oxidised acids the petroleum spirit used should have S.G. 0·695–0·705 and B.Pt., 65°–95°, and that it should be as free as possible from unsaturated and benzene hydrocarbons, but Goldschmidt and Weiss (*ibid.*, 1921, 40, 396A) do not agree with this latter suggestion and state that any kind of petroleum spirit may be used. It is now possible to remove the whole of the solvent by careful treatment so that the extracted oil no longer gives reactions for carbon bisulphide.

Canzoneri (*Analyst*, 1915, 40, 399) states that extracted oils are now neutralised and decolourised by a patent process of esterification. The substances produced by this process have a pleasant odour and are completely saponifiable; it is soluble in alcohol, ether, carbon bisulphide and rapidly oxidises to form a viscous liquid. Samples has S.G. 0·901–0·9055; iodine value, 73–75·2; index of refraction (no temperature given), 1·4603.

Villavecchia is of opinion that, in general, an olive oil may be regarded as pure when it is coloured only pale yellow by Heydenreich's, Hauchecorne's or Brulle's reagent, has a saponification number not less than 192 and an iodine number not exceeding 83, and does not contain arachidic, lignoceric or erucic acid. An oil with a saponification number less than 192 and an iodine number above 83, but of normal behaviour as regards all the other tests, may be regarded as genuine.

The official Italian methods give for olive oil the limits indicated above for the different characters, excepting that the solidifying temperature is given as 2–6, the refractometer index at 40°, 1·4618–1·4623, and the iodine number as 79–90. They give further: Reichert-Meissl number 0·3; Hehner number 95·5–96·2; acetyl number 4–10; absolute iodine number 95–104; unsaponifiable residue, which should be constituted of minimum traces of phytosterol scarcely sufficient for the reaction with chloroform and sulphuric acid (100 grms. of the oil yield 0·45–0·47 grm. of crude phytosterol, whilst sesamé and cotton-seed oils give respectively 1·28 and 1·20 grm.)

The following remarks by Shelley (*Analyst*, 1924, 49, 335) in connection with two abnormal samples of olive oil should be of interest:

" *Sample No.* 1.—This had an extremely bitter taste, not unlike that of strychnine, and left a burning sensation in the throat.

" On analysis it gave the following figures: Sp. gr., 0·9156; saponification value, 194·4; iodine value, 79·9; free fatty acids, 0·4 per cent.; and $n_D^{40°}$, 1·4613; arachis and cotton-seed oils, absent; Baudouin's test (furfurol and hydrochloric acid modification) a distinct red, changing to olive-green.

" The bitterness and reaction in Baudouin's test seemed the only abnormalities. On referring to Thorpe's *Dictionary of Applied Chemistry*, Vol. IV, p. 701, I found the following:

> " ' According to Bourquilot and Vintilesco, olives contain a glucoside, oleoeuropein—a yellow powder with bitter taste—hydrolysable by emulsin, which is present in the fruit, leaves and bark.' And under *Olive Oil*, p. 702: ' Olives intended for oil production are gathered just before maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully-ripe or over-ripe fruits.'

" As it seemed possible that the two bodies might be present in this oil, I shook up some of the oil with water (A) and kept the mixture at a temperature of 80° F., together with some of the oil (B). At the end of ten days

the separated oil from sample A was free from bitterness and acridity, and was bland and of a beautiful golden colour.

" The analytical figures were very similar to those of the untreated oil, excepting that the free acidity was slightly reduced, and that Baudouin's reaction was almost negative (a very slight and fugitive pink).

" Sample B was still bitter and acrid after 14 days in the incubator.

" The writer suggests that the abnormal climatic conditions in Spain last year were not favourable to complete hydrolysis taking place before the fruit was pressed (hence the bitterness) and that emulsin and oleoeuropein being present in some stage of hydrolysis, other than the bitter one, may account for the fact that some olive oils give a positive reaction in Baudouin's test.

" *Sample No.* 2. This oil was reported upon as containing 30 to 40 per cent. of arachis oil, this conclusion, presumably, having been arrived at from its behaviour in the British Pharmacopœia test. The writer has frequently experienced difficulty with this test during the winter months, when the temperature during the 24 hours sometimes falls many degrees below freezing-point. As a result of some tests, he would suggest that the B.P. instruction should be altered to read ' and kept at a temperature of 15·5° C. for 24 hours.'

" Some of the oil in question, afterwards reported upon as free from arachis oil (A), some mixed with 15 per cent. of nut oil (B), and some with 10 per cent. of nut oil (C), were subjected to the B.P. test, with this difference, that all three were kept in an incubator at a temperature of 15·5° C. for the required period. The following results were obtained:

" A, entirely free from crystals; B, a heavy deposit of crystals; C, a very few crystals (so few as to leave one doubtful).

" On putting flasks A and C into a water-bath and keeping them at a temperature of 12° C. for an hour, no crystals were deposited in A, but C (with 10 per cent. of nut oil) gave a heavy deposit."

Hydrogenated Olive Oil.—Myddleton and Barry give the composition of the fatty acids of a hardened olive oil of iodine value 53·0 (iodine value of original oil, 82·5) as palmitic, 14·6; stearic, 24·0; oleic, 26·0; linolic, 0·0; " new acids of hydrogenation," 35·4.

" Lipolytic Enzymes in Olive Oil." Rector, *J.S.C.I.*, 1920, 39, 304A.

" The Bacteriology of Canned Olives." Koser, *Analyst*, 1921, 46, 103.

" The Action of Driers on Olive Oil." Mackey and Ingle, *J.S.C.I.*, 1916, 35, 454.

" The Dry Distillation of Olive Residues." Basanta, *J.S.C.I.*, 1924, 43, B525.

CHAPTER XX

VEGETABLE FATS

Bassia (Indian Illipé) Tallow

Bassia tallow or Indian Illipé tallow is obtained from several species of *Bassia*, the fat of which is very similar although according to some writers the true Indian Illipé butter is obtained from *B. longifolia*, whilst fat from the other species of *Bassia* is only commercially sold as Indian Illipé. Careful distinction should be made between the Illipé fat from India which is the product of one or more of the *Bassia* species and some commercial Illipé fat which is really Borneo tallow obtained from species of *Shorea* and described on page 282. It will be noticed that the iodine value of the latter is distinctly lower than that of Bassia tallow.

B. longifolia occurs in the southern parts of India whilst *B. latifolia*, which is also known as Mowrah (Mohwrah or Morah) butter, occurs mostly in the north of India. *B. butyracea* occurs in the Himalayas. *B. djave* is found in West Africa, *B. mottleyana* in Sarawak, whilst *B. parkii* (shea butter) is plentiful in West Africa and the Soudan. It will be convenient to deal here with *B. latifolia*, *B. longifolia* and *B. butyracea* (frequently known as Phulwar butter), which are the species usually described as being the sources of Indian Illipé or Bassia tallow, whilst leaving the others for description below under separate heads.

The seeds vary somewhat in size according to the particular source but usually weigh about 1 grm. or less and contain some 50 per cent. of fat. According to Sudborough, Watson and Chandorkar, who describe the oil as Mohua oil (*J.S.C.I.*, 1923, 42, 562A), crude oils with acidities below 13 are readily refined by alkali treatment although the loss reaches 18 per cent. The neutralised oil (which is yellow) may be bleached colourless by vegetable charcoal and deodorised by superheated steam under reduced pressure. When subsequently hydrogenated a practically colourless product is obtained which, by adding 20 per cent. of ghee, may be used as a ghee substitute. According to these authors the oil consists of the glycerides of stearic, oleic and palmitic acids; free palmitic acid may be isolated from the press cake (Winterstein, *J.S.C.I.*, 1919, 38, 544A).

The cake is said to contain a saponin-like substance (*Biochem. J.*, 1910, 4, 93) with marked physiological activity when subcutaneously injected, but apparently without action when fed to cattle. The changes which the seeds undergo after plucking have been studied by G. J. Fowler and T. Dinanath (*J.S.C.I.*, 1923, 42, 986A), who state that " the fruits, if plucked when near the ripening stage, contain small amounts of sucrose and reducing sugars, which increase considerably if the fruits are allowed to remain at room temperature for a day or two. The quantity of sucrose is at a maximum on the third day after plucking, after which decomposition sets in and the sucrose and total fermentable sugars decrease. The starch content decreases very rapidly in the first two days after plucking, and the tannins are almost constant in quantity till the third day, when they begin to disappear. These changes in the composition of the fruit can be explained by assuming that the starch is broken down by the enzymes present, amylase being very

active during the first day, invertase during the first two days, and maltase during the first three days, after which their activity gradually diminishes."

According to P. Berg and J. Angerhausen (*Analyst*, 1914, 39, 310) the fat contains about 2 per cent. of unsaponifiable matter which has $[\alpha]_D$ +27·1° in chloroformic solution, the bulk of this consists of a substance which is insoluble in alcohol and which has $[\alpha]_D$ +35°. It is stated that this unsaponifiable substance is not phytosterol and that it is not precipitated by digitonin, and a suggested method for the detection of Bassia fat depends upon solution of the unsaponifiable matter from 100 grms. of the oil in a small quantity of ether and pouring the ethereal solution into excess (about 100 c.c.) of absolute alcohol (a turbidity here suggests the presence of Bassia fat). The solution is filtered, partially evaporated to remove ether and digitonin added. The digitonin precipitate is separated, the solution is evaporated and the residue extracted with ether when the excess of digitonin remains insoluble. The ethereal solution is evaporated and the optical rotation of the residue determined—most fats, it is stated, give an inactive residue, while Bassia fat (and shea butter) yield a residue having $[\alpha]_D$ +35°.

The unsaponifiable matter has been further studied by S. Kobayashi (*J.S.C.I.*, 1922, 41, 987A), who found that it consisted of a light yellow solid with an aromatic odour and the following characters: M.Pt., 148°–154°; iodine value, 178·5; saponif. value after acetylation, 83·7; ether-soluble bromide about 71 per cent.; bromine content, 67·30 per cent. It gave a white precipitate of digitonide with an alcoholic solution of digitonin and the bromide became blackish-brown at 150° and turned black at 165° without melting. The unsaponifiable matter was treated with hot 95 per cent. alcohol, and from the insoluble matter a highly unsaturated hydrocarbon was isolated by repeated recrystallisation from ether. This hydrocarbon, illipene, $C_{32}H_{56}$, has M.Pt. 64·5°, iodine value 382·5, and gives 312·2 per cent. of ether-insoluble bromide (67·46 per cent. Br.). It is optically inactive and boils above 315° at 2·5 mm. pressure. The higher alcohols in the unsaponifiable matter were freed from sterols by means of digitonin and when fractionated by repeated recrystallisation from acetone gave the following compounds: $C_{21}H_{38}O$, microscopical silky needles, M.Pt., 196°–197°; iodine value 114·9 and saponif. value after acetylation, 150·7°; $C_{31}H_{56}O$; silver-white crystals, M.Pt., 186°–186·5°; iodine value, 100·2; $C_{27}H_{48}O$; silver-white grains, M.Pt., 159°–160°; iodine value, 82·3; $C_{21}H_{36}O$; light-yellow needles, M.Pt. 125°–135°; iodine value, 100·2; saponif. value after acetylation, 132·5°.

It would thus appear that the work of Berg and Angerhausen either refers to fat from a different source or that it needs very careful checking, but as the sample examined by Kobayashi contained as much as 8·6 per cent. of unsaponifiable matter it cannot be considered as above suspicion.

The composition of the fat of *B. latifolia* (Mowrah-seed oil) has been determined by Gill and Shah (*J.O.F.I.*, 1925, 2, 46), who worked with a sample having sap. value, 206·5; iodine value, 57·9; Reichert value, 0·7; Polenske value, 0·9; acid value, 14·2; unsaponifiable matter, 0·8 per cent. They found glycerides of the following acids : Clupanodonic, trace; linolic, 13·3; oleic, 40·2; stearic, 2·0; palmitic, 26·6; myristic, 16·1 per cent.

Table CXXVII.—Characteristics of Bassia Tallow

Bassia Latifolia

Observer.	S.G.	M.Pt. °C.	Acid Value.	Sap. Value.	Iodine Value.	R.M.	n_D^{40}.	Unsap. per cent.
Crossley and Le Sueur .	0·894–0·898 at 100°/100°	23–29	4·8–21·2	187·4–194·0	53·4–67·8	0·4–0·9	1·4605–1·4610	..
Lewkowitsch . . .	..	25–31	34–40	187·6 196·2	52·6 63·9	1·6 1·7	..	2·34
[1] Imperial Institute . .	0·857–0·870 100°/15°	..	20–34·8	188·3 199·8	56·7 76.8	0·2 1.0	..	1·7–3·5
[2] Sudborough, etc. . .	0·925 at 15°	..	..	196·5	59·5	1·4	1·4605	..
Bolton and Revis . .	0·860 99°/15°	..	49	192·2	59·4	..	1·4577	..

[1] *Analyst*, 1912, 37, 54; 1914, 39, 134. [2] *J.S.C.I.*, 1923, 42, 562 A.

Bassia Longifolia

Observer.	S.G. 100°/15°.	M.Pt. °C.	Sap. Value.	I.V.	Acid Value.	R.M.	n_D^{40}.	Titre. °C.	Unsap. per cent.
Lewkowitsch . . .	..	42	187·4–188·5	58–64	..	1·4	..	40	2·6
Imperial Institute .	0·856–0·864	..	191·5–202·7	54·8–61·2	5·0–25·7	2·3–3·6	..	36–45	1·4–2·1
Sprinkmeyer and Diedrichs *	..	..	190·0–192·7	60·2–64·2	1·3–58·1	1·7 1·7	1·4598–1·4621	..	1·8
Bolton and Revis . .	0·862	..	189·8	62·6	6·5	..	1·4589	..	..

* *Analyst*, 1912, 37, 349.

Bassia Butyracea

Observer.	S.G. 100°/15°.	M.Pt. °C.	Sap. Value.	R.M.	I.V.	n_D^{40}.	Acid Value	Titre. °C.	Unsap. per cent.
Lewkowitsch . .	..	39–51	190·8–194·6	0·4–1·3	41·2–42·1	1·4552–1·4582	..	..	2·2
Imperial Institute .	0·856–0·862	..	195·3 200·0	0·0–4·3	39·6 42·7	..	20·7 &59·6	48·2 51·5	2·2 2·8
Diedrichs * . .	..	..	..	3·1	47·7 50·6	1·4642 1·4659	1·0 50·0	.. ..	2·2 5·3
Bolton and Revis .	..	..	188·2	1·3	42·6	1·4578	17	..	1·4

* *J.S.C.I.*, 1914, 33, 1098.

The figures of Jean (*Analyst*, 1906, 31, 262), who gives saponification value, 175 and iodine value, 20, must obviously be taken with reserve as they are quite different from those of all other observers. It will be observed that the fats of *B. longifolia* and *B. latifolia* are very similar, whilst that from *B. butyracea* has a considerably lower iodine value. Bolton and Revis (*Fatty Foods*, p. 183 *et seq.*) suggest that the two former be known as " Longifolia fat " and " Latifolia fat " respectively, and the suggestion is a useful one, although as the two are so nearly alike in properties and value not much difficulty arises from their confusion. For the biogenesis of Bassia fat see Fowler and Dinanath (*J.S.C.I.*, 1925, 44, B178).

Borneo Tallow

Borneo tallow is derived chiefly from the kernels of *Shorea stenoptera*, Burck., but the seeds of a number of other species of *Shorea*, such as *S. ghysvertiana*, *S. aptera*, *S. robusta* are also used as a source of this oil as also are those of *Isoptera borniensis*, Scheff., *Hopea aspera*, De Vriese and *Pentacme siamensis*, Kury. All these sources belong to the family *Dipterocarpeæ*. According to the Imperial Institute (*J.S.C.I.*, 1915, 34, 1213) the kernels of these species came from Borneo, Java, and Sumatra, and occur in commerce under the name of " Illipé " nuts—the grades most commonly met with being " large black Pontianæ illipé nuts " and " large Pontianæ or Sarawak illipé nuts without guarantee of colour."

Bolton and Pelly (*Oils, Fats, Waxes and Resins*, London, 1924) state that the black nuts are considered to be the best and contain nearly 70 per cent. of fat, whilst the brown ones as a rule have only 48 to 50 per cent. The trees bear fruit after about twelve years and the fruits are collected as they drop. No real cultivation of the trees can be said to take place and the fruiting depends largely on the season.

Several methods have been used by the natives for preparing the oil. The most usual one is to allow the nuts to stand in a damp place so that the shells crack and allow the easy removal of the kernels. This method, however, yields a poorer product of bad colour. In Borneo the nuts are completely immersed in water and allowed to remain there for some thirty to forty days, this process of immersion being considered to act in some way as a precaution against attacks by insects. The kernels are usually exported as such after drying in the sun, only that oil being expressed locally which is required by the natives for their own use. The fat is known locally as Tangkawang or Tankawang fat.

The various constants which have been observed for this oil are set out in Table CXXVIII.

The fat is remarkably similar to cacao butter in all its properties, in fact so much so that it was at one time practically impossible to distinguish mixtures of these fats from either of the original substances. Tate and Pooley (*Analyst*, 1921, 46, 229) have, however, working in the Government Laboratory, made suggestions which are not without interest, and, although other workers have apparently not been quite so successful, yet the method is the only one which is at all likely to give useful results. On account of the chief importance of this fat being used as a cacao substitute full details of the methods of examination are given under this latter fat on page 308.

Cacao butter substitutes of this nature are known to some extent in commerce as " Beurre Vert " or " Green butters." These were at one time frequently green in colour probably caused by the presence of chlorophyll, although artificially coloured fats are not unknown. The green colouring

matter is, however, by no means always present so that a " Green butter " may have the same appearance as cacao butter.

TABLE CXXVIII.—CONSTANTS OF BORNEO TALLOW

Observer.	S.G. 99°/15°.	M.Pt. °C.	I.V.	Sap. Value.	n_D^{40}.	Acid Value.	Titre. °C.	M.Pt. Acids. °C.	Unsap. per cent.
Tate and Pooley .	0·857–0·858	30·3–34·7	27·4–33·4	..	1·4561–1·4573	..	..	52·0–54·1	..
Sachs	..	37·5	30–31	192·4–196	..	..	52·0	53·5	..
[1] Sprinkmeyer and Diedrichs . .	..	28·7	29·7	196·6	1·4571	1·0	..	..	0·5
[2] Imperial Institute	0·852–0·856	29–33	31·0–31·8	190·7–194·4	..	8·5–35	53·0–53·5	..	..
Brooks	0·854–0·856	28–37	30·0–31·5	190·2–192·1	1·4559–1·4567	11·3–24·7	51–53	56	0·3–0·5

[1] *Analyst*, 1912, 37, 349. [2] *J.S.C.I.*, 1915, 34, 1213.

Species of *Palaquium* are also frequently known as Borneo tallow. The fat is described by Lewkowitsch as Surin fat (*Analyst*, 1906, 31, 2) which is the native name for the fat from at least one species of *Palaquium*. The sample examined by Lewkowitsch was described as " Minyak surin, from Perak, Straits Settlement." The fat, after filtering, had the following characteristics:

Fat—

Specific gravity at 60° (water at 60° = 1) . . .	0·9021
Solidifying-point, commences to solidify at °C. .	48·9
,, ,, solid at °C.	43·9
Melting-point, °C.	56·1
Saponification value	179·5
Unsaponifiable matter, per cent.	4·54
Iodine value	42·31
Reichert-Wollny value	0·55
Acid value	68

Fatty acids—

Solidifying-point, °C.	59·1
Mean molecular weight	284·9
Stearic acid (of melting-point, 67·8°), per cent. . .	58·2

Lewkowitsch states that the seeds of *P. pisang* are supposed to contain 45 per cent. of a bitter yellowish fat known in commerce under the name " Balam tallow," whilst from *P. oleosum*, a white sweetish fat (" Suntei

tallow ") is expressed. The species of *Palaquium* examined by Bontoux had the following characteristics:

Oil—

Solidifying-point, °C.	30
Melting-point, °C.	38·5
Saponification value	177·7–182·3
Iodine value	48·2–57·2

Fatty acids—

Titre test, °C.	54·8
Melting-point, °C.	57
Neutralisation value	181·1–182·8

P. oblongifolium yields a hard white fat different from the other species of *Palaquium*, known as " Njatuo tallow " and similar to the fat from *Shorea* species; it is used in Borneo as an edible fat. The following characteristics have been observed for this fat:

TABLE CXXIX.—CHARACTERISTICS OF PALAQUIUM

Observer.	M.Pt. °C.	Acid Value.	Sap. Value.	I.V.	% Unsap.	M.Pt. Acids. °C.
De Jongh and Tromp.	40	4·2	201·5	34·3	..	..
[1] Imperial Institute	38	7·0	190·4	35·9	1·0	58·0

[1] *Analyst*, 1916, 41, 7.

OIL FROM SPECIES OF GARCINIA

The *Garcinia* species contain several plants, the seeds of which yield useful oils, many of which are suitable for edible purposes. The oils so prepared have not been studied extensively, but various more or less isolated investigations have been carried through; these are given below under the various headings.

G. balansæ.—The seeds of this species, which is stated to be synonymous with *G. tonkinensis*, have been examined by C. Grimme (*Analyst*, 1911, 36, 21), who found 63·4 per cent. of a dark-brown fluid oil in the kernels and by F. Heim (*J.S.C.I.*, 1918, 37, 63A) who states that the tree matures in 8 to 10 years and would yield a full crop of seed only after 20 years. The seeds have long been considered of value in the Tonkin district and are used for the extraction of burning oil which, however, is mixed with an oleo-resin containing a small proportion of ethereal oil of agreeable odour. The seed weighs about 2 to 3 grms. and consists of about 95 per cent. kernel. The following characteristics have been observed:

TABLE CXXX.—CHARACTERISTICS OF OIL FROM G. BALANSÆ

Observer.	S.G. 15°.	Sol. Pt.	I.V.	Acid Val.	n_D^{40}.	Titre. °C.	M.Pt. Acid. °C.	Unsap. %.	Sap. Val.
Grimme . .	0·913	8·6	86·2	19·9	1·4682	30·3	32·5	4·2	176·3
Heim . .	..	..	67·1	93	..	..	22	..	198

The oil which is known as Cay-doc oil in Annam was described as from *G. balansæ* by Grimme and from *G. tonkinensis* by Heinn, which sources are considered to be synonymous, but the figures obtained by these two observers would not lead one to this conclusion.

G. cambogia.—These seeds were found by Rau and Simonsen (*J.S.C.I.*, 1922, 41, 912A) to yield 31 per cent. of fat which resembled that from other species of *Garcinia*. These authors state that the fat consists for the most part of the glycerides of stearic and oleic acids and that it is an excellent edible fat.

G. Conrauana.—The fruit of this tree is known as " bitter kola seeds " but contains no caffeine and is quite different from *Cola acuminata* the true kola nut. It has been examined by the Imperial Institute (*Analyst*, 1912, 37, 258).

G. echinocarpa.—The thick oil from this species is locally known in India as " Madol oil "(*Bull.* Imp. Inst., June 1901) where it is used as a burning oil and also as a vermifuge.

G. indica.—This plant which is stated to be synonymous with *G. purpurea* is the source of Goa butter which is also known as Kokum butter and Mangosteen oil. The seeds contain about 25 per cent. of fat, which is usually obtained by the crude native method of boiling the oil out with water and skimming from the surface. The fat consists for the most part of glycerides of oleic and stearic acid, probably largely of oleo-distearin. The oil is used for edible purposes and as an adulterant of ghee. The following characteristics have been observed :

TABLE CXXXI.—CHARACTERISTICS OF OIL FROM G. INDICA

Observer.	Sol. Pt. °C.	M.Pt. °C.	Sap. Value.	I.V.	R.M.	n^{40}.	Titre. °C.	M.Pt. Acids. °C.
Heise	38	40	191·3	33·1	1·5	1·4574	..	61
Crossley & Le Sueur	..	42	186·8	34·2	0·1	1·4565	..	..
Hooper	..	43	191·5	25·0	1·0	..	..	61

G. morella.—This is the source of the so-called Gamboge butter. The tree grows in Mysore and on the Western Coast of India. The fat is variously known as " Murga fat " and " Gurgi fat " by the natives. Both fats have been examined by D. Hooper (*Analyst*, 1907, 32, 358), who con-

siders that the fat consists largely of dioleo-stearine. Hooper's results are given in the following table:

TABLE CXXXII.—CHARACTERISTICS OF OIL FROM G. MORELLA

	Garcinia Morella (Murga Fat).	*Garcinia Morella* (Gurgi Fat).
Specific gravity at 50°/50° . .	0·900	0·902
Melting-point, °C.	37°	33·5°
Acid value	3·49	13·79
Saponification value	198·20	194·74
Iodine value	53·72	55·46
Reichert-Meissl value . . .	0·69	0·62
Fatty acids per cent. . . .	94·89	95·20
Melting-point of fatty acids, °C.	56·0 C.	55·0 C.

G. pictoria.—This tree grows in Western Mysore and the fat extracted from the seeds is used as an edible fat by the poorer classes, whilst inferior qualities are used as a burning oil. The oil has not apparently been fully examined.

ILLIPÉ FAT

At one time it was considered that the term Illipé fat referred solely to the product of *Bassia longifolia*, L., a tree which occurs to a considerable extent in India. Whatever truth there may have been in this statement at one time is uncertain but in any case there is no doubt but that the term Illipé fat is used indiscriminately in connection not only with species of Bassia but also of *Palaquium* and *Shorea*. A. W. Knapp (*Analyst*, 1921, 46, 236) states that the name Illipé fat is meaningless, whilst Bolton and Pelly (*Oils, Fats, Waxes and Resins*, London, 1924, page 94) express the following opinions:

> A great deal of confusion exists as to the trade and botanical names of this and other somewhat similar fats which are indiscriminately referred to under the indefinite name of " illipé."
>
> The seeds to which the name illipé is given fall into three main classes:
>
> 1. The Bassia seeds of India (Natural Order, *Sapotaceæ*), including *Bassia latifolia*, which yields " mowra " fat, *B. longifolia* and *B. butyracea*, yielding " phulwa " butter.
>
> 2. The " siak " seeds, species of *Palaquium*, small nuts also belonging to the *Sapotaceæ*, sometimes called " small siak nuts."
>
> 3. The *Shorea* seeds. These are often known as " Large Pontianak " or " Sarawak " (towns in Borneo) " illipé nuts " to distinguish them from Class 2.
>
> It is thus obvious that great confusion has resulted from so wide an application of the term illipé, and the indiscriminate use of the word is greatly to be deprecated;

whilst Georgi (*J.S.C.I.*, 1924, 43, B525) states that " the term ' illipé ' includes the true illipé nuts of India (*Bassia*, sp. N.O., *sapotaceæ*); the nuts

of Malaya, Borneo, Sumatra and Java, from various species, principally *Shorea* of the N.O. *Dipterocarpeæ*, and the Siak nuts of Malaya (*Palaquium*, sp. N.O. *Sapotaceæ*). Fat expressed from Malayan illipé nuts is indiscriminately known as Borneo tallow, but local trade is mostly in the nuts themselves, and a large proportion of the exports passes through Singapore. The nuts are marketed as illipé nuts with a prefix denoting the district of origin, e.g., Sarawak, Pontianak."

It is obvious that this term Illipé fat should no longer be used in any but a general sense, so that the various fats which have from time to time passed under this name will therefore be described under names by which they are more particularly known. See Borneo Tallow, Shea Butter, Mowrah-seed oil, Phulwara butter, etc. Cf. Surin fat, Adjab fat, Katio oil, etc.

Japan Tallow

Japan tallow is extensively, and at one time was exclusively, known as japan-wax on account of its physical resemblance to the waxes. It is, however, a true fat consisting for the most part of glycerides and is, therefore, better described as japan tallow.

It is obtained from the berries of various species of *Rhus* (the sumach tree) such as *R. succedaneo*, *R. acuminator*, *R. vernicifera*, *R. sylvestris*. The trees which are grown in China, Japan and India are chiefly valued as a source of lacquer. The oil is prepared by crushing the matured berries and separating the kernels. The crushed mass is then pressed in the usual way. Tsujimoto (quoted by Lewkowitsch) states that with the growing demand for japan-wax the aim has been to increase the output; this is accomplished by mixing the press residue, or even the ground berries, with about 10 per cent. of perilla oil and again pressing. This accounts, of course, for the somewhat wide variations of the commercial fats both in melting-points and in other characteristics. The crude wax is melted and strained and then allowed to drop into cold water which is kept stirred so that the fat solidifies in thin flakes. The flakes so produced are then exposed in shallow trays to the action of the sun and air, being occasionally sprinkled with water and moved over. The bleached material is finally remelted and cast into blocks. The berries contain about 25 per cent. of fat, the yield obtained under commercial conditions depending, of course, on the methods used for expression.

The fat is a hard and brittle wax-like solid, pale-yellow or light-brown in colour, usually having a somewhat pronounced and characteristic odour. It is soluble in the usual fat solvents and also in boiling alcohol from which latter it crystallises almost completely on cooling.

The fatty acids present consist for the most part of palmitic acid. The composition has been studied by Geitel and Van der Want (*J.S.C.I.*, 1900, 19, 356); Schaal (*ibid.*, 1908, 27, 28); Matthes and Heintz (*ibid.*, 1910, 29, 222); and by Tassilly (*ibid.*, 1911, 30, 907). The last worker found large quantities of palmitic acid, small quantities (about 1 per cent.) of dibasic acids (japanic acid and its homologues) and perlagonic acid and traces of stearic and oleic acids, together with an acid having the formula, $C_{15}H_{30}O_2$ or $(C_{15}H_{30}O_2)_2$. About 5 per cent. of soluble acids have been found which, it is possible, are formed during bleaching.

Adulteration is occasionally practised but is not difficult to detect. The points to watch are freedom from water, a high melting-point and a high iodine value as adulterants are likely to lower the former and decrease the latter. The melting-point should be over 50°, the saponification value

about 220 and the iodine value usually less than 10 although addition of perilla oil and variations in the method of expression will tend to increase this figure which has been found by some observers as high as 15. The acid value of commercial samples varies widely from 5 to 25 or more, but should be, as a rule, less than 20. The unsaponifiable matter varies between 0·7 and 1·7 per cent., whilst the titre test usually gives about 60° or rather less. The specific gravities given by various observers are somewhat divergent, but usually it is not much less than unity. According to Dieterich, japan tallow has been used to some extent as an adulterant of beef tallow. He states that this admixture may be detected by heating 26 grms. of the sample with 75 c.c. of petroleum spirit and allowing to cool. In the case of pure tallow the solution remains clear, whilst in the presence of japan tallow a turbidity is produced. A further test also proposed by Dieterich, is to boil 0·5 grm. of the fat with 20 c.c. of a saturated solution of borax and then cool the mixture. In the presence of japan tallow an emulsion is produced whilst the aqueous solution remains clear in the presence of pure beef tallow.

J. B. M'Nair (*J.S.C.I.*, 1918, 37, 430A) states that fats isolated from *Rhus laurina* and *R. diversiloba* had the following constants respectively: Sp. gr. (18·5° C.), 0·8987, 0·9872; solubility, 136, 170 mg. per litre in 95 per cent. alcohol at 20° C.; iodine value (Hübl) 11·44, 8·79; saponif. value, 157·1, 220·6; M.Pt., 74°, 53° C. The substances appear to be more similar to japan-wax than to any other fat. A decrease in the poisonous properties of the fruit of *R. diversiloba* occurs simultaneously with an increase in the fat content, but this does not appear to be due to the conversion of the poison into fat.

Macassar Oil

This oil is produced from the seeds of *Schleichera trijuga*, Willd., which have been described by Bolton and Jesson (*Analyst*, 1915, 40, 3) in the following way:

> " *Schleichera trijuga*, Willd. (Nat. Ord., *Sapindaceæ*).—This genus is confined to India (Central Provinces, West Peninsula, and Burma) and the Malayan region, where the nuts are variously known as ' Kusambi nuts,' ' Pacca,' etc. The tree is the lac tree of Kosumba (' Ceylon oak '), and the oil is there known as kon or kusum oil, being said to be the original Macassar oil. Fruit 1½ to 2 cm. long usually echinate, ovate-oblong or spherical, dark reddish-brown. Seeds 1 or 2 in number, 1 to 1½ cm. long, testa light yellowish brown; they are said (Brandis, *Indian Trees*, p. 190) ' to be enclosed in a succulent arillus of pleasantly acid taste.' The endosperm in the dried condition is yellow. A pale straw-coloured, semi-solid oil is contained in the kernels, which, it will be noted, gives a very high Reichert-Meissl value, and also a high Kirschner value. These figures, taken in conjunction with the low Polenske value, might render the oil difficult to detect if used as a butter adulterant, were it not for a peculiar colour reaction noticeable on saponification with alcoholic potash, and for certain other analytical differences."

The seeds weigh between 0·5 and 1 grm. each and consist of about 40 per cent. shells and 60 per cent. kernel, the latter containing some 60 to 70 per cent. of oil. The following characteristics have been observed for the oil:

TABLE CXXXIII.—CHARACTERISTICS OF MACASSAR OIL

Observer.	Sol. Pt. °C.	Sap. Value.	I.V.	R.M.	Pol.	n^{40}.	Titre. C°.	Acid Value.	Unsap. per cent.
Lewkowitsch . .	10	215–230	48–69	9·0	..	..	52	6·2–35·4	3·1
Bolton and Jesson	20	227	54·5	16·0	0·3	1·4597	..	15·8	..

MAFURA TALLOW

This fat is obtained in the seeds of *Trichilia emetica*, Vahl, of which *Mafureira oleifera* is said to be a synonym. It has been described at some length by De Negri and Fabris, the Imperial Institute, Daniel and M'Crae, and more recently by J. Wolff.

Daniel and M'Crae state that two products are produced, the first by boiling the seeds and water and skimming the oil from the surface—mafura oil, and the second, by crushing and pressing the seeds—mafura tallow, which is said to be poisonous. Daniel and M'Crae found the following characteristics (*Analyst*, 1908, 33, 276):

TABLE CXXXIV.—CHARACTERISTICS OF MAFURA TALLOW (DANIEL AND M'CRAE)

	Mafura Oil.	Mafura Tallow.
Fat—		
Specific gravity at 15°/15° C.	0·931	..
,, ,, 30°/15° C.	0·920	0·909
,, ,, 40°/15° C.	0·913	0·902
Melting-point, °C.	..	29·5°–38° C.
Saponification value	202·5	201·
Iodine value	66	43·5
Reichert-Wollny value	2·0	1·3
Saponification value of acetylated fat . .	235	218
True acetyl value	36·5	16
Butyro-refractometer: " degrees "—		
,, ,, at 20° C. . . .	65·6	..
,, ,, at 30° C. . . .	60·1	..
,, ,, at 40° C. . . .	54·6	47·3
Unsaponifiable, per cent.	0·8	1·2
Free fatty acids, per cent.	8·9	14·7
Insoluble fatty acids—		
Specific gravity at 92°/15° C.	0·854	0·843
Solidifying-point, °C.	44·2° C.	52·1° C.
Neutralisation value	201	204
Saponification value	206	205
Iodine value	68	46
Butyro-refractometer: " degrees " . .	37·2 at 50° C.	26·3 at 57° C.

The results of De Negri and Fabris and of the Imperial Institute are thus summarised by Daniel and M'Crae:

"I. De Negri and Fabris, prepared in laboratory; II. De Negri and Fabris, commercial sample; III. Imperial Institute, from entire nuts; IV. Imperial Institute, from kernels only; I*a*. Mixed fatty acids from I; II*a*. Mixed fatty acids from II."

Sample.	Mt.Pt. °C.	Sol. Pt. °C.	Acid Value.	Sap. Value.	Iodine Value.
I . . .	35–41	33–25	..	200·08	44·85
II . . .	35·5–42	37–30	..	220·96	46·14
III . .	37	20–25	52·5	..	55·8
IV* . .	40	25–30	42·4	..	47·8
I*a* . . .	51–54	47–44	..	..	46·92
II*a* . .	52–55	48–44	..	..	48·19

J. Wolff (*J.S.C.I.*, 1922, 41, 21A) states that the fat is soft and yellow or brownish with a pleasant nutty odour which may be removed by steam distillation. He found the following characteristics:

Acid value	31·0–32·2
Unsaponifiable matter	1·1–1·5
Saponification value	202–207
Iodine value (Wijs)	45·1–46
„ „ (Hübl-Waller)	49·6–52
Reichert value	3·0–3·4
Polenske value	2·7
Titre, °C.	42·5–43·5

The fat of the seeds of *T. subcordata* has been examined by J. Ostling (*J.S.C.I.*, 1914, 33, 147) who states that the seeds yield 55·7 per cent. of a fat consisting mostly of palmitin, stearin and a smaller quantity of olein with some glycerides of volatile acids. He observed the following characteristics:

Melting-point, °C.	45
Solidifying-point, °C.	24–30
Acid value	39·6
Saponification value	201·5
Iodine value	39·9
Reichert value	3·3
Titre, °C.	51·5
Iodine value of acids	42·5

Malabar Tallow

Malabar tallow is obtained from the seeds of *Vateria indica*, L., a large evergreen tree growing in India and the East Indies, which is used in India as an edible fat. The fat which is free from odour and flavour has been

* Cf. *Analyst*, 1909, 34, 164.

examined by, among others, Crossley and Le Sueur (*J.S.C.I.*, 1898, 17, 991), who found the following characteristics:

Specific gravity, 100°/100°	0·890–0·891
Melting-point, °C.	37–37·5
Saponification value	188·7–189·3
Iodine value	37·8–39·6
Reichert value	0·2–0·4

Oils from the Myristicaceæ

A number of plants belonging to the Natural Order *Myristicaceæ* have seeds which contain notable proportions of oil. These oils, which are at present of no great commercial importance, are dealt with shortly below, under each individual plant.

Nutmeg butter.—Nutmeg butter is obtained from the seeds of *Myristica officinalis*, the common nutmeg. The amount available is small and the fat is of no great importance, being used chiefly for medicinal purposes. The fat has been examined at some length by Power and Salway (*J.C.S.*, 1908, 93, 1653), and the following characteristics have been observed:

Table CXXXV.—Characteristics of Nutmeg Butter

Observer.	M.Pt. °C.	Sap. Value.	I.V.	R.M.	n^{40}.	Titre. °C.	M.Pt. Acids. °C.
Dieterich	42–51	153·5–178	40·1–52	..	..	..	..
Spaeth	..	169·1–173	75·6–80·8	4·2	..	..	..
Other observers	43–50	154–161	48–85	2·1	1·4662–1·4704	35–45	42–49

The oil as expressed contains up to 10 per cent. of ethereal oil, so that the figures obtained on examination will depend on the amount of this substance present. The fat from *Myristica argentea*, according to Lewkowitsch, contains no ethereal oil, but has the same characteristics as above; it is known as "Papua nutmeg butter" or "Macassar nutmeg butter." The fat from *Myristica malabarica* differs considerable from these having M.Pt., 31°, saponification value, 189·4–191·4, iodine value, 50·4–53·5, and refractive index at 40°, 1·4580 to 1·4586 (Spaeth).

Kombo Butter.—This fat is obtained from the seeds of *M. angolensis* which is known by various native names depending upon the district from which it is obtained. The seeds have been described by the Imperial Institute who state that they are of the size of a small, oval plum, weighing in the dry state about 4 grms. They are similar in appearance to nutmegs but contain no ethereal oil. The kernels yielded 54 per cent. of a hard fat to petroleum ether which had the following somewhat curious characteristics:

TABLE CXXXVI.—CHARACTERISTICS OF KOMBO BUTTER

	Crude Fat.	Refined Fat.
Specific gravity at 99°/15°	0·887	..
Acid value	26·5	nil.
Saponification value	255·0	183·0
Iodine value	65·4	33·7
Titre test	37	37·6

An oil obtained from the seeds of *M. canarica* by Hooper which was light-brown in colour and crystalline in nature had the following characteristics:

Fat—

Melting-point	37·5°
Saponification value	215·02
Iodine value	26·64
Acid value	37·08

Fatty acids—

Melting-point	41°
Neutralisation value	217·53

Ucuhuba Fat.—This fat is obtained from the seeds of *M. bicuhyba* (J. Wolff, *J.S.C.I.*, 1922, 41, 21A) which is apparently synonymous with *Virola bicuhyba* (Bolton and Hewer, *Analyst*, 1917, 42, 35). These latter authors state that the seeds alone seem to be indistinguishable either by appearance or analysis from those of *Virola venezuelensis*, Warb., known under the name " Cuajo," and equally so from those of *Myristicia surinamensis*, though the seeds of *M. guatemalensis* (*Fatty Foods*, p. 272) usually have a lower content of fat, which gives slightly different constants.

Owing to the large variety of *Myristica* species, there is some confusion due to the overlapping of the botanical names given to the same member by different botanists, and the line of demarcation is neither botanically nor analytically clear. *M. malabarica*, however, may be distinguished by its long-shaped seeds, while *M. canarica*, also found in Brazil, usually has a high content of resinous matter which is difficult to separate from the oil.

All the above-named seeds have a more or less pronounced arillus, which contains an essential oil, producing a characteristic odour. In the case of Ucuhuba seeds the proportion of ethereal oil is very small, and the fatty matter, if not too acid, may be refined to an almost odourless and neutral state, and a valuable fat thereby obtained. Acid and decomposed fats provide an excellent candle material on distillation.

The fat is dark coloured when freshly pressed from the whole seed on account of the colouring matter contained in the shell which causes a characteristic blood-red colouration with sulphuric acid. The seeds weigh about 1–3 grms. and consist of about 82 per cent. of kernel which contains some 70 per cent. of oil. The following characteristics have been observed:

TABLE CXXXVII.—CHARACTERISTICS OF UCUHUBA FAT

Observer.	Sol. Pt. °C.	Sap. Value.	I.V.	Acid Value.	Unsap. per cent.
Bolton and Hewer	40·0	220·3	14·1	35	3·2
Wolff	..	224·0	12·7	30·7	2·5

The oils from *Virola guatemalensis* and *V. venezuelensis* have been examined by Grimme with the following results (*J.S.C.I.*, 1910, 29, 1318):

Source.	Yield.*	M.Pt. °C.	n^{40}.	Acid Value.	Sap. Value.	I.V.	M.Pt. Acids °C.	I.V. Acids.	Unsap. per cent.
V. guatemalensis	60·7	41·0	1·4576	28·0	244·0	13·8	38·0	15·6	1·13
V. venezuelensis	74·7	47·0	1·4541	19·1	221·5	12·4	43·0	12·9	0·86

Myristica Platysperma.—The oil of *Myristica platysperma*, Spruce (synonym *Osteophlœum platyspermum*, Warb.) was apparently first described by E. M. Jesson (*J.S.C.I.*, 1915, 34, 499), who states that the tree is indigenous to N.W. Brazil, that the inner shell of the fruit is brittle and easily crushed and that the kernels of one sample contained 55·2 per cent. of a white crystalline fat having very little odour. According to Bolton and Hewer (*Analyst*, 1917, 42, 35) the seed has the characteristic structure of the *Myristicaceæ* and consists of 45 per cent. of shell and 55 per cent. of kernel. The kernel contains 59·3 per cent. of a pale creamy-white very hard and brittle fat which would command a high price. The following characteristics have been observed:

TABLE CXXXVIII.—EXAMINATION OF OIL FROM MYRISTICA PLATYSPERMA

Observer.	M.Pt. °C.	Sol. Pt. °C.	Acid Value.	I.V.	Sap. Value.	n^{40}.
Jesson	43	39	10·5	6·3	240·2	1·4501
Bolton and Hewer . .	42·5	39·8	7·4	5·0	239·5	1·4502

Otaba Butter.—This fat is obtained from the spherical seeds of *Myristica otaba*, a forest tree growing in the mountains of Columbia. The seeds have been examined at the Imperial Institute (*Analyst*, 1921, 46, 51) the report of which states that the seeds are about 2 cm. in diameter and consist of 30 per cent. shell and 70 per cent. kernel. The kernels yield 7·2 per cent.

* Yield of oil from kernels.

of a colourless volatile oil on steam distillation, whilst the residue, after drying, yielded 67·3 per cent. of a fat having the characteristics given in the table below. The fat has also been examined by Baughman, Jamieson and Brauns (*Analyst*, 1921, 46, 138), who found in the oil 9·3 per cent. of essential oil and 20·4 per cent. of other unsaponifiable matter. The fixed oil consisted of the glycerides of lauric, (15·1); myristic, (52·2); palmitic, (0·2); and oleic acids (3·9); and the unsaponifiable constituents, besides the essential oil, consisted of a viscous yellow mass (11·0 per cent.) and of the isomeric otobite and iso-otobite, $C_{20}H_{20}O_4$ (9·4 per cent. together). Otobite (M.Pt., 137°–138°), and iso-otobite (M.Pt. 106°–108°) both give with concentrated sulphuric acid a pink colouration, which becomes very intense on standing and persists for days. Addition of several drops of concentrated sulphuric acid to glacial acetic acid solution of either compound (phytosterol test) gradually produces a pink colouration, which turns somewhat purple after some hours and persists for some days. Attempts to obtain acetyl derivatives or to methylate the compounds with methyl sulphate were unsuccessful, whilst treatment with alcoholic potassium hydroxide solution and fusion with potassium hydroxide were without effect. Otobite contains one methoxyl group in the molecule, but iso-otobite none. Both compounds form pentabromides, $C_{20}H_{20}O_4Br_5$ (M.Pt. 190° and 191° respectively).

The following characteristics have been observed:

TABLE CXXXIX.—CHARACTERISTICS OF OTABA BUTTER

Observer.	M.Pt. °C.	Acid Value.	Sap. Value.	I.V.	Titre. °C.	n^{40}.
Imperial Institute .	37·8	16·8	198·9	20·1	37·2	..
Baughman, etc. . .	34·0	..	185·0	54·0	..	1·4710

SAWARRI FAT

According to Lewkowitsch (*J.S.C.I.*, 1890, 9, 844) sawarri fat (also known as Suari or Surahwa and imported under the name of bitter nuts) is contained in the seeds of *Caryocar butyrosum*, Willd., synonymous terms for which are *C. tomentosum* and *C. nuciferum*.

The seeds contain 60 per cent. of fat which is excellent for edible purposes. The following characteristics were determined by Lewkowitsch:

Melting-point, °C.	29·5–35·5
Saponification value	199·5
Iodine value	49·5
Reichert value	0·7
Titre, °C.	46
Melting-point of acids	48·3–50

The seeds of a *Caryocar* species, probably *C. amygdaliferum* or *C. brasiliense*, have been examined by Bolton and Hewer (*Analyst*, 1917, 42, 44), who describe the seeds and their fat in the following way:

" The seeds consist of a brown shell, smooth and shiny inside and raised into irregular protuberances all over the outside. This encloses an oily

kernel, white in colour and covered with a thin brown skin. The kernels are edible, and are described by Bentley as ' probably the most agreeable of all the nut kind.' "

The fat, which is a firm, brittle solid, is snow-white in colour, practically odourless, and with a very pleasant taste. It is an edible fat *par excellence* but, owing to the fact that it does not " mould " well, is unsuitable alone as a cacao butter substitute; but if mixed with softer fats the difficulty might be overcome. Needless to say, it would serve, in admixture with suitable oils, as a margarine fat, lard substitute or baking fat.

The seeds weigh about 20 grms. and contain 23 per cent. of a kernel which contains 70 per cent. of oil.

These authors observed the following characteristics:

Melting-point, °C.	37·0
Solidifying-point, °C.	28·6
Saponification value	197·6
Iodine value	41·9
Acid value	0·2
n^{40}	1·4567

Shea Butter

Shea butter (also known as kerité butter, although some writers state that there is a distinction between them, cf. Southcombe, *J.S.C.I.*, 1909, 28, 499), is obtained from the fruits of *Butyrospernum parkii* or *Bassia parkii*. This tree occurs in large quantities in West Africa and in the Soudan and is considered by the natives to be a valuable source of oil. The fruits consist of about one-third shell and two-thirds kernel, the percentage of fat in the kernel varying from about 40 to 55 or more.

The oil contains a large proportion of stearic acid (34–37 per cent. Lewkowitsch, 30–35 per cent. Southcombe) and oleic acid (60 per cent. Southcombe), whilst much smaller quantities of lauric, etc., may be present. According to A. Hébert (*J.S.C.I.*, 1911, 30, 496) the native method of separating the fat is to remove the bulk of the fruit pulp and to bury the residue in the earth, where a partial fermentation liberates the kernels from their envelopes. The kernels are dried, first in the sun and then at a gentle heat over little stoves, after which they are ground between stones to a paste, and the fat extracted by treatment with boiling water. This author's experiments have shown that the yield of fat (23 to 25·4 per cent.) and its chemical and physical constants are practically the same, whether obtained from sun-dried or from roasted kernels.

According to Berg and Angerhausen (*Analyst*, 1914, 39, 440) shea butter contains an unsaponifiable substance which is not precipitated by digitonin and which has $[\alpha]_D + 38°$ and this may be used as a method of detection. This work is not supported by that of S. Kobayashi (*J.S.C.I.*, 1922, 41, 987A) which is described on page 280 under Bassia tallow. Further work along these lines is desirable.

The rather large amount * of unsaponifiable matter contained in the oil (figures as high as 9 per cent. have been recorded) has been a somewhat serious objection to the use of this oil, particularly for edible purposes, but in the latest methods of refining a portion of this can be removed, and a useful edible fat is now prepared on a fairly large scale from those seeds which originally contain a smaller amount.

* Cf. J. Wolff (*J.S.C.I.*, 1922, 41, 21A).

TABLE CXL.—EXAMINATION OF SHEA BUTTER

Observer.	S.G. 100°/15°.	M.Pt. °C.	Acid Value.	Sap. Value.	I.V.	R.M.	Acid Value.	n_D^{40}.	Titre. °C.	Uns pe cen
Southcombe .	..	[1]25–27	..	175·3 177·1	66–67·1	..	..	..	..	·
,, .	..	27–30	..	173·9 183·4	54·8 57·5	..	..	..	..	·
,, .	..	[3]29	..	178·7	57·6	1·2	26·2	..	..	·
Imperial Institute	[4]0·862 [2]0·869	.. ..	18·0 7·6	179·0 181·5	58·7 62·0	.. 2·6	.. ..	.. ..	52 ..	1· 6·
[5] Sprinkmeyer & Diedrichs	..	43·4 45·2	9·0 66·6	177·0 188·0	54·4 60·0	1·4	..	1·4647 1·4663	..	3· 10·
Imperial Institute	[6]0·862	..	..	179·0 184·6	54·0 58·0	..	..	..	51·8 53·2	1·
,,	[7]0·859 0·869	..	..	180·2–184·0	55·8 62·9	..	..	..	..	4· 7·
Bolton & Revis.	..	37–42	Upwards of 4·0	180·0 190·0	57·6 63·0	..	..	1·4629 1·4636	..	5· 9·

[1] From Soudan. [2] From Nigeria. [3] Prepared by natives. [4] From Lagos. [5] 13 samples. [6] Prepared by natives. [7] Extracted in laboratory by petroleum ether.

As in the case of coconut oil this material is not infrequently divided into oleine and stearine; the following table contains figures on these two products determined by Bolton and Revis:

TABLE CXLI.—CHARACTERISTICS OF SHEA NUT "STEARINE" AND "OLEINE"

Estimation.	Shea Nut "Stearine."	Shea Nut "Oleine."
M.Pt., incipient fusion, °C.	40·0	..
M.Pt., complete fusion, °C.	55·5	..
Solidifying-point, °C.	34·2	24·0
Saponification value	179·7	181·6
Ref. index at 40° (Zeiss butyro-refrac.)	52·7	58·7
Iodine value	51·9	62·3
Free fatty acids	3·4%	5·89%
Unsaponifiable matter	6·25%	7·72%
Reichert-Meissl value	..	2·60
Polenske value	..	0·72

Various other species of *Bassia* and allied plants are used by the natives as sources of oil for edible and other purposes and have, to a certain extent, become articles of commerce; these are shortly described below:

Adjab Fat.—This fat is obtained from the seeds of *Mimusops njave* or *Djave*, which seems to be synonymous with *Bassia toxisperma* or *Bassia djave*, a tree found in West Africa which yields, like the other members of this family, gutta-percha. In the Gold Coast the nuts are known as Abeku, Bako or Mahogany nuts. The fat is variously described as Njave, Djave, Noumgon or Adjab fat. The seeds were found by Freundlich (*Analyst*, 1908, 33, 330) to contain 4·5 per cent. of a volatile oil and 65 per cent. of a soft light-brown fat of the consistency of lard. This author suggests the following reaction as typical of the oil, but there would seem to be need of confirmation of this, particularly in the case of refined samples: "When a solution of the fat in hot alcoholic potassium hydroxide solution is mixed with ammonia solution and cooled it yields a jelly-like mass which is readily filtered. On the addition of hydrochloric acid to the filtrate which contains the soluble potassium soaps the fatty acids separate, whilst the aqueous layer assumes a violet-pink colouration."

According to C. A. Mitchell the fat has not yet been used for edible purposes except by the natives, largely due to the fact that traces of hydrocyanic acid are usually present, but which, of course, are readily removed. According to Fickendey the fresh seeds contain an extremely poisonous saponin which is either removed from the oil or retained in the press cakes.

The nuts are similar in shape to shea nuts (usually weighing about 15 grms.) and consist of about two-thirds kernel. The kernels contain some 60 per cent. of a white or yellowish-white solid fat. The following characteristics have been observed:

TABLE CXLII.—CHARACTERISTICS OF ADJAB FAT

Observer	Sol. Pt. °C.	Acid Value.	Sap. Value.	I.V.	R.M.	n_D^{40}.	Titre. °C.	Unsap. per cent.
[1] Freundlich . .	28	13·8	182·5	56·0	0·7	..	46	2·2
[2] Imperial Institute .	..	25·3	187·6	56·2	0·0	..	47·8	2·6
Fickendey . . .	..	18·2	188·6	57·2	0·8	..	46	2·6
Wagner and Oestermann . .	..	..	186·7	56·2	0·8	..	46·3	..
Bolton and Revis .	21	18·5	184·2	65·1	..	1·4605	47·8	3·9
Wedenmeyer . .	..	38·1	185·3	56·1	1·2	1·4607	44·1	3·7
[3] Sprinkmeyer and Diedrichs . . .	39·3	129·0	182·8	59·0	2·5	1·4609	..	7·4

[1] *Analyst*, 1908, 33, 330. [2] *Analyst*, 1909, 34, 164. [3] *Analyst*, 1912, 37, 349. Polenske, 0·5.

The oil of *Mimusops elengi* has been studied by Rau and Simonsen (*J.S.C.I.*, 1922, 41, 902A), who found that the seeds yielded 16 per cent. of an oil consisting of the glycerides of oleic, stearic and palmitic acids and of an unidentified saturated acid which was possibly behenic acid.

Katio Oil.—Katio oil (also known as Katiau or Kachiau) is obtained from the seeds of *Bassia Mottleyana*, C. B. Clarke. The seeds have been examined by Brooks (*Analyst*, 1909, 39, 207), the Imperial Institute (*J.S.C.I.*, 1913, 32, 201), and Bolton and Revis. The seeds weigh about one-third of a grm. and consist of about one-third shell and two-thirds kernel, the latter containing 47 to 56 per cent. of fat. The fat is soft in texture and of a pale-yellow or greenish-yellow colour containing about 75 per cent. of oleine and 25 per cent. of stearine.

" Brooks describes the oil prepared by the Dyaks as having a pleasant odour of almonds, which neither the Imperial Institute nor Bolton and Revis have found to be true of oils which were extracted from the seeds in the laboratory. The native-prepared fat was, however, found to have a pronounced smell of almonds, and this was investigated by the Imperial Institute, who found no prussic acid, but proved the presence of benzaldehyde, which they suggest had been added for the purpose of flavouring or scenting the oil." C. A. Mitchell.

The characteristics given in the following table have been observed by the workers named :

TABLE CXLIII.—COMPARISON OF ADJAB FATS

Source.	Observer.	S.G. 15°/15°.	Sol. Pt. °C.	Acid Value.	Sap. Value.	I.V.	n_D^{40}.	R.M.	Titre. °C.	Unsap. per cent
Prepared by natives	Brooks	0·917	14·0	1·8	189·5	63·2	1·4616	..	..	0·41
	Imperial Institute	..	..	2·3	191·5	65·0	..	0·6	36·3	..
	Bolton and Revis	0·917	15·0	1·7	188·9	66·5	..	..	..	..
Extracted from seeds	Imperial Institute	..	..	77·9	191·0	65·0	..	0·8	36·4	..
	Bolton and Revis	..	..	13·8	192·1	65·2	1·4609	..	..	..

Lamy Butter.—This fat is obtained from the fat of *Pentadesma butyracea*, which occurs in West Africa. It is variously known as Lamy butter, Kanja butter, Kanga butter and Sierra Leone butter. The nuts have been examined at the Imperial Institute (*Analyst*, 1918, 43, 352) and it is stated that they are derived from a large tree generally known as the " butter or tallow tree," but have been forwarded to this country under the name of " shea butter seeds," from which, however, they are quite distinct. The kernels are large, irregular, and dark reddish-brown, and when dried to contain 12·4 per cent. of moisture, yielded 36·6 per cent. of soft pale-yellow fat having a slight but agreeable odour.

Other observers have found that the seeds contain from 45–50 per cent. of fat.

The following characteristics have been observed by various workers:

TABLE CXLIV.—CHARACTERISTICS OF LAMY BUTTER

Observer.	S G. 100°/15°.	M.Pt. °C.	Acid Value.	Sap. Value.	I.V.	n_D^{40}.	R.M.	M.Pt. Acids.	Titre. °C.	Unsap. per cent.
Grimme . .	..	42	26·4	197·0	42·3	1·4563	..	57	54·5	0·92
Hébert . .	..	32	16·0	199·0	68·5	..	0·3	60	..	..
Imperial Institute . .	0·857–0·859	33	3·1 17·4	186·0 191·7	41·8 46·5	..	0·0	..	50·7	1·7

[1] *Analyst*, 1911, 36, 21. [2] *J.S.C.I.*, 1911, 30, 497. [3] *Analyst*, 1909, 34, 164; 1914, 39, 134; 1918, 43, 352.

A similar fat may be obtained from the seeds of *Pentadesma kerstingii*. This has been examined by Wagner, etc. (*J.S.C.I.*, 1915, 34, 366), who found that the seeds contained 41·5 per cent. of a fat having the following constants:

Melting-point, °C.	38–39
Acid value	12·4
Saponification value	192
Iodine value	45·9
Reichert value	0·2
Polenske value	0·4
n_D^{40}	1·4562
Unsaponifiable matter, per cent.	0·6

STILLINGIA TALLOW

Stillingia tallow coats the seeds of the tree *Stillingia sebifera*, which is a native of China and which is cultivated there and in India. Various other plants are also used as sources of a similar product which is known generally as Chinese vegetable tallow. The fat is produced either from the whole seed when the tallow is obtained mixed with the oil (Stillingia oil, see page 184) or the tallow and oil are obtained separately. When the former method is used and the whole seed is crushed, a considerably softer fat than the true tallow is obtained. In the case of the latter method the seeds may be passed between rollers which break off the outer coating of fat without crushing the seed or, alternatively, they are heated with steam in perforated cylinders or trays when the fat melts, runs off and is collected. The fat is exported from China (as the fat and not as the seeds) in moderately large quantities and is used chiefly in the manufacture of soap and candles. It is not impossible to use the oil as an edible oil when suitably purified but it soon deteriorates, becoming bitter in taste and disagreeable in odour. It has a somewhat peculiar property of expanding with great force at the congelation-point.

The composition of the fat has not been determined with certainty, but it would appear from the work of Maskelyne, Hehner and Mitchell, and Kliment that the bulk of the fatty acids consists of palmitic and oleic. In Kliment's opinion the fat itself consists principally of oleodipalmitin. The constants obtained for this fat by various observers are contained in the following the table:

TABLE CXLV.—EXAMINATION OF STILLINGIA TALLOW

Observer.	M.Pt. °C.	Sol. Pt °C.	Sap. Value.	I.V.	R.M.	n^{40}.	Acid Value.	Pol.	Unsap. per cent.	T°
Lewkowitsch . .	43–46	24–26	199–204	32–38	0·7	1·4546	..	..	..	
[1] Sprinkmeyer and Diedrichs . .	41·3 42·5	26·7 27·5	200·9 202·4	39·5 40·5	0·2–0·8	1·4570–1·4574	0·6–0·9	0·5–0·6	0·30 0·49	
[2] Diedrichs . .	..	..	206	29·8	0·9	1·4556	7·0	..	..	

[1] *Analyst*, 1912, 37, 349; cf. *ibid.*, 1896, 21, 328. [2] *J.S.C.I.*, 1914, 33, 1098; cf. *ibid.*, 1897, 16, 339.

TUCAN OIL

This oil is obtained from the fibrous pulp of *Astrocaryum vulgare*, Mart., a plant distantly allied to the African oil palm. The palm which grows to a height of 30 to 50 feet is found in large quantities in Central America. The fruit weighs from 15 to 20 grms. and consists of pulp 30, shell, 50 kernels, 20. The kernels weigh about 3·5 grms. and measure 18–25 mm. in. length and 13–18 mm. in diameter. The pulp contains about 35 per cent, of oil and the kernel about 45 per cent. The kernel oil is described on page 353. The oil is similar to palm oil and is prepared in a like manner. The following characteristics have been observed:

TABLE CXLVI.—CHARACTERISTICS OF TUCAN OIL

Observer.	S.G. 15°.	Sap. Value.	I.V.	M.Pt.	n_D^{40}.	Titre. °C.	Unsap. Per cent.
Bontoux	0·916	197	75–76	..	..	32	..
[1] Bolton and Hewer.	..	222·2	46·4	35	1·4610	..	0·75

[1] *Analyst*, 1917, 42, 35.

CHAPTER XXI

CACAO BUTTER

SOURCE.—Cacao butter is obtained from cacao beans, a portion of the fruit of the "cocoa" tree *Theobroma cacao*, L. This tree, and the products derived therefrom, has been described at length by various authors, details of which are given below on page 303; the present writer is indebted to Mr A. W. Knapp for permission to use some of the information contained in his book, *Cocoa and Chocolate: Their History from Plantation to Consumer*. For further details this most interesting work should be consulted.

According to Knapp the original habitat of the cacao tree was in the country watered by the Amazon and the Orinoco. The plant was brought to Europe by Columbus and others of the early explorers. The cultivation of the tree was carried out by the American Indians, who caused it to be spread over the whole tropical belt of the American continent and cultivated it as far north as Mexico. Cacao was planted by the Spaniards in Trinidad in 1525, in 1834 it was taken to Ceylon. In 1880 some cacao beans were taken to the Gold Coast, in 1891 the first bag of cacao weighing 80 pounds was exported, whilst in 1915 the amount had increased to 120 million pounds. The tree can only grow at tropical temperatures, and when shielded from the wind and unimpaired by drought. The ideal spot is the secluded vale, and whilst in Venezuela there are plantations up to 2000 feet above sea-level, it cannot generally be profitably cultivated above 1000 feet. The cacao tree is not unlike the usual type which grows in the temperate zone. It is usually about twenty feet in height when fully grown and begins to bear in its fourth or fifth year. The leaves, which cover the tree the whole year round, are about a foot in length and four inches in breadth. The flowers, which always grow alongside the fully-developed fruits, are small, being not more than half an inch in diameter at their widest part when fully developed. The fruit, which is connected directly to the trunk on a short thick stalk, may be anything in shape from a melon to a stumpy, irregular cucumber, according to the botanic variety. The intermediate shape is like a lemon, with furrows from end to end. The pod is covered with a thick, almost woody rind and contains thirty to forty beans covered with juicy pulp.

When the pods are quite ripe they are harvested by removal with sharp cutlasses or by means of a hook-knife fixed to the end of a long pole. The pods are cut open with some sharp instrument by hand and the beans are removed. These beans are then moist and full of juice—in order to render them fit for travel a process of fermentation is necessary. The nature and amount of this fermentation varies with the different varieties of cacao, but in general the beans are stacked in heaps or placed in boxes, covered to conserve the heat produced during fermentation and left to ferment, but are well mixed from time to time to produce a uniform product. (Cf. F. Hardy, *J.S.C.I.*, 1925, 44, 305T.) When fermentation is complete, which is judged by the appearance, the beans * are dried, care being taken that they become sufficiently dry to prevent the formation of mould without making the husks so brittle that they will become broken in transit. In Venezuela and formerly in Trinidad † the beans are covered with earth or clay which

* Washing to remove pulp is practised in Ceylon and Java.

† Claying is now forbidden in Trinidad.

usually has a deep red colour—this is considered to be objectionable, it serves no useful purpose and may easily degenerate into adulteration.

TABLE CXLVII.—COMPARISON OF CACAO BEANS

Kind.	Average Weight of one Bean.	Number of Beans to the pound.
Grenada . . .	1·0 grm.	450
Para	1·0 ,,	450
Bahia	1·1 ,,	410
Accra	1·2 ,,	380
Trinidad . . .	1·2 ,,	380
Cameroons . .	1·2 ,,	380
Ceylon . . .	1·2 ,,	380
Caracas . . .	1·3 ,,	350
Machala . . .	1·4 ,,	330
Arriba	1·5 ,,	300
Carupano . . .	1·6 ,,	280

The beans on arrival in Europe are sorted and cleaned in the usual way and then roasted in order to develop the characteristic aroma. "After roasting, the shell is brittle and has been quite freed from the cotyledons or kernel. The kernel has become glossy and friable and chocolate-brown in colour, and it crushes readily between the fingers into small angular fragments (the 'nibs' of commerce), giving off during the breaking down a rich warm odour of chocolate. The roasted beans are then broken and the husk and germ removed, after which the nib is ground to an impalpable paste, which on cooling sets to a hard brown mass.

"This 'mass' may be used for the production of either 'cocoa' or chocolate. When part of the fat (cacao butter) is *taken away* the residue may be made to yield cocoa. When sugar and cacao butter are *added* it yields eating chocolate. Thus the two industries are seen to be interdependent, the cacao butter which is pressed out of the mass in the manufacture of cocoa being used up in the production of chocolate." The cacao butter is removed by expression in some type of oil press. "The liquefied

TABLE CXLVIII.—EFFECT OF ROASTING ON CACAO BEANS

Constituents.	Grenada Bean (with shell).		Trinidad Bean (without shell).	
	Raw.	Roast.	Raw.	Roast.
Moisture	6·32	3·10	6·67	4·45
Fat	46·50	46·96	54·60	55·70
Nitrogen	1·96	1·86	2·28	2·32
Fibre	3·60	3·90	2·45	2·48
Total ash	2·86	3·12	2·87	2·73
Siliceous matter	0·10	0·12	0·03	0·08
Soluble ash	1·26	1·44	0·94	0·95
Alkalinity as K_2O	0·68	0·75	0·42	0·43
Cold-water extract	13·50	12·90	12·73	12·00

cacao bean put into the pots contains 45–55 per cent. of butter, whilst the 'cocoa' press cake taken out usually contains only 25–30 per cent."

Table CLXVIII, due to Booth, Cribb and Richards (*Analyst*, 1909, 34, 134), shows the differences in the composition of cacao bean which are produced on roasting.

Examination of Cacao Preparations.—The complete description of the ordinary methods of examination lies outside the scope of this work but reference may be made for this purpose to the following papers:

"The Amount of Cacao Butter Contained in the Cacao Bean." Davies and M'Lellen. *J.S.C.I.*, 1904, 23, 480.

"The Determination of Fat in Cocoa and Chocolate." A. Kreutz. *Analyst*, 1908, 33, 320; 1909, 34, 19.

"The Detection of Added Alkali in Cocoa." K. Farnsteiner. *Analyst*, 1909, 34, 52.

"The Quantity of Fat in Commercial Cocoas." A. Beythien. *Analyst*, 1909, 34, 52.

"The Composition and Methods of Analysis of Chocolate." Booth, Cribb and Richards. *Analyst*, 1909, 34, 134.

"The Theobromine Content of Cocoa and Cacao Beans." A. Kreutz. *Analyst*, 1909, 34, 20, 319.

"Method of Determination of Oxalic Acid in Cocoa." J. M. Albahary. *Analyst*, 1909, 34, 396.

"The Analysis of Milk or Cream Chocolate." Baier and Neumann. *Analyst*, 1909, 34, 439.

"The Determination of Xanthin Bases in Cocoa." A. Prochnow. *Analyst*, 1910, 35, 125.

"Estimation of Cacao Husks in Cocoa." C. Ulrich. *Analyst*, 1912, 37, 52.

"Determination of Fat in Cocoa." O. Richter. *Analyst*, 1912, 37, 495.

"The Essential Oil of Cacao." Bainbridge and Davies. *J.C.S.*, 1912, 101, 2209.

"Detection and Determination of Xanthin Bases in Cacao, etc. Camilla and Pertusi. *Analyst*, 1913, 38, 60.

"The Presence of Copper in Cacao." C. Formenti. *Analyst*, 1913, 38, 145.

"Report on Cacao and Cacao Products." W. L. Dubois. *Analyst*, 1914, 39, 123.

"The Composition of Cacao Seeds and 'Stabilised' Cacao." L. Reutter. *Analyst*, 1914, 39, 171, 434.

"The Composition of the Radicles of Cacao Beans." E. P. Haussler. *Analyst*, 1914, 39, 308.

"The Determination of Starch in Cacao by Means of Taka-Diastase." *Analyst*, 1915, 40, 429.

"Note on the Determination of Theobromine." Radford and Brewer. *Analyst*, 1917, 42, 274.

"The Application of Science to Cacao Production." A. W. Knapp. *J.S.C.I.*, Rev., 1918, 37, 468.

"The Separation and Uses of Cacao Shell." A. W. Knapp. *J.S.C.I.*, 1918, 37, 240T.

"The Estimation of Cacao Shell." A. W. Knapp and B. G. M'Lellan. *Analyst*, 1919, 44, 2.

"Analyses of 'Cocoa Teas.'" Baker and Hulton. *Analyst*, 1918, 43, 189.

" The Estimation of Shell in Cacao and Cacao Products." Baker and Hulton. *Analyst*, 1918, 43, 197.

" The Determination of Theobromine in Cacao and its Products." R. V. Wadsworth. *Analyst*, 1920, 45, 133; 1921, 46, 32; 1922, 47, 152. Cf. G. Cappelli, *J.S.C.I.*, 1924, 885B.

" The Setting of Cacao Butter, with Special Reference to the Development of ' Bloom ' in Chocolate." *J.S.C.I.*, 1925, 44, 77T.

" The Composition of Cacao Germs." F. Hartel. *J.S.C.I.*, 1924, 43, B570.

" The Determination of Fat in Cacao Products." L. Feldstein. *J.S.C.I.*, 1924, 43, 885B.

" The Examination of Cacao." *J.S.C.I.*, 1924, 43, 1026B.

Properties of Cacao Butter.—Cacao butter as freshly obtained is a pale yellow, brittle, wax-like solid which melts at about 33° to an amber-coloured liquid. It possesses strongly the characteristic odour of cacao which is very persistent; the taste is bland and agreeable. It is possible to bleach and deodorise the substance until the product is without colour and odour, but this is only occasionally done for pharmaceutical purposes in cases where the natural odour is objectionable. The substance possesses excellent keeping qualities, so much so that they have become almost legendary, thus " when pure, it has the peculiar property of not becoming rancid, however long it may be kept." W. H. Johnson. Cacao butter will, however, become rancid like any other fat if kept under conditions favourable to such a change (Lewkowitsch, *J.S.C.I.*, 1899, 18, 557). When exposed to light the yellow colour disappears somewhat quickly and the substance becomes quite white. The great value of cacao butter for pharmaceutical purposes is that, although hard and brittle at ordinary temperatures, it melts at lower than body temperature.

The occurrence of a considerable growth of mould in the centre of cacao butter has been observed by Batten and Bywaters (*J.S.C.I.*, 1918, 37, 242T) in a case where a small amount of water was present. The following remarks of J. Allan (*J.S.C.I.*, 1918, 37, 243T) are of interest and importance in this connection: " There was one point in connection with the storage of fats which accentuated the difficulties arising from the presence in them even of very small quantities of water. It was well known that the fats which were solid at ordinary temperatures had a great tendency during solidification, particularly if it were prolonged, to develop a condition which was known as ' seed,' i.e., the mass became more or less granulated. Usually in solidification of fat under these conditions, the portion which solidified first possessed little or no structure; the granular structure, which was generally in the centre, was almost akin to crystallisation. At the same time the water in the fat tended to pass towards the centre of the mass, resulting in a higher percentage of water in that part. Consequently the mere estimation of the original water content of the fat was not a safeguard against such conditions as had been put forward in the paper. If it was intended to store fats of this kind for any length of time, care should be taken to avoid this granulated structure. It was not infrequent to find it in parcels of high-grade tallow arriving from Australia or America, even though care had been taken during cooling and packing to get them as nearly as possible homogeneous in texture, and red, green and black moulds were often found in the centre of the packages."

During the European War, 1914–1918, the manufacture of chocolates was greatly restricted in this country so that large quantities of cacao butter

were set free on the market. On account of the shortage of edible fats of all kinds many attempts were made, and in some cases with no little success, to use the cacao butter, which was then sold at a comparatively low price, for culinary purposes. The dietetic qualities of the fat have been studied by Gardner and Fox (*J.S.C.I.*, 1920, 39, 277A), who found that it is rather less digestible than butter and that beyond a slight laxative action no undesirable physiological effects were observed to follow the administration of considerable quantities of the fat.

Composition.—Cacao butter consists largely of the glycerides of stearic and oleic acids with smaller quantities of other solid and liquid acids. Various investigations have been made into the composition of this substance, the earliest of which appears to be that of Kingzett (*J.C.S.*, 1878, 33, 38), but the first really complete statement is that due to Knapp (*J.S.C.I.*, 1923, 42, 508A) who found the fat to consist of the glycerides of stearic acid (40 per cent.), oleic acid (31 per cent.), of linolic, lauric and myristic acids in small amounts and of capric, caproic, butyric, acetic and formic acids in traces. With regard to the presence of the latter acids it should be noted that the Reichert value is low (usually 1·0 or less and frequently below 0·5) so that if all of these acids are actually present they can only be so in extremely small amounts. The subject has been reinvestigated by Morgan and Bowen (*J.S.C.I.*, 1924, 43, 346T) who were unable to isolate any acid higher than stearic acid, from which it will be seen that the composition is by no means definitely settled and that more work on the subject is desirable.

The unsaponifiable matter has been investigated by Matthes and Rohdich (*Analyst*, 1908, 33, 93). These authors failed to isolate any constituent to which the peculiar flavour of the cacao could be attributed. The unsaponifiable matter from this quantity of fat amounted to 28 grms., consisting of a pleasant-smelling oil with an odour of hyacinth and 22 grms. of " crude phytosterol." From the latter were isolated a hydrocarbon, $C_{30}H_{48}$, identical with amyriline, a phytosterol which combines with 2 atoms of bromine by addition, identical with the stigmasterol prepared from Calabar beans by Windaus, and a phytosterol which combines with 1 atom of bromine, identical with the sitosterol of Calabar beans. This phytosterol possessed the properties of the " ordinary " phytosterol, which forms the unsaponifiable residue of most vegetable fats.

An extended investigation into the glycerides present has been undertaken by Amberger and Bauch (*Analyst*, 1925, 50, 77). These authors have shown it to consist of the glycerides of oleic, stearic and palmitic acids, the acids being present in the following proportions: Oleic acid, 43–45 per cent.; palmitic acid, 23–25 per cent.; and stearic acid, 31–33 per cent.; no acids of higher molecular weight could be detected. The following proportions of glycerides were found: Tristearin, 0·02; β-palmito-α-α-distearin, 0·03; oleo-α-β-distearin, 24·92; oleo-β-palmito-stearin, 20·29; and α-palmito-α-β-diolein, 54·74 per cent. A sample of the fat which had been hydrogenated in the presence of palladium had an iodine value of 5·9 and M.Pt., 60·5 C., and contained 77 per cent. of palmitic acid with 22·7 per cent. of stearic acid, and the separated glycerides consisted of tristearin, 25; β-palmito-α-α-distearin, 20; and α-palmito-α-β-distearin, 55 per cent.

The Characteristics of Cacao Butter.—Cacao butter is apparently very uniform in composition so that samples from different sources yield characteristics which do not vary greatly among themselves. As in the case of nearly all fats many of the older determinations are, for many reasons, unreliable, so that they are not reproduced here; one of the reasons for this is that the methods of manufacture having become standardised, the product

is now of a more uniform composition than it was years ago. Knapp (*Cocoa and Chocolate*, page 159; *J.S.C.I.*, 1923, 42, 508A) finds that the acid value of commercial samples varies from 1 to 4—the average figure is about 1 to 1·5. The unsaponifiable matter varies from 0·3 to 0·8 per cent., and the ash 0·02 to 0·05 per cent. The following may be taken as average characteristics (largely according to Knapp, *loc. cit.*):

Specific gravity,* 15/15	0·990–998
Melting-point	32–34 †
Titre	49–50
Iodine value	34–40
Saponification value	192–198
Reichert value	1·0
Polenske value	0·5
Kirschner value	0·5
n^{40}	1·4565–1·4570
M.Pt. fatty acids	48·5–50·0

C. Ulrich (*Analyst*, 1912, 37, 52) found that the iodine value of the fat of roasted beans ranged from 32·2–35·6 (mean 34·1), whilst in that of the unroasted beans the limits were 34·7–36·5 (mean 35·5). W. Vaubel (*J.S.C.I.*, 1924, 43, B524) has stated that the characteristics change considerably during the course of manufacture. Thus in one case the crude fat extracted from the raw beans had saponification value, 229·7; iodine value, 48·2;‡ and M.Pt. of fatty acids, 45–49, whilst that in the manufactured had saponification value, 190 and iodine value, 43·8. This author suggests that the commonly accepted extremes for the characteristics of pure cacao butter should be extended, but this would not appear necessary as, apart from the fact that these figures have apparently been obtained on quite a few samples, cacao butter from raw beans is not a commercial substance. It may be useful, however, to bear this point in mind in the case of apparently adulterated samples. The fat from alkalised "cocoa" has the same melting-point and iodine value as normal cacao butter (Strube, *Analyst*, 1908, 33, 188).

Cacao Husk Fat.—The fat extracted from the husks differs considerably from true cacao butter. The husks contain about 4 per cent. of fat having the following characteristics when extracted with ether (Galanos, *J.S.C.I.*, 1924, 43, B1019):

Saponification value	180
Iodine value	39
Reichert value	8·2
Polenske value	0·4
n^{40}	1·4633

Prochnov and Velmans found that the iodine value of the husk fat was 43·2 to 46·2, but C. Ulrich (*Analyst*, 1912, 37, 52) does not confirm this, and finds indeed the fat in the unroasted husks to have iodine value 36 to 38, whilst that from the roasted shells has the value 34·8 to 37·9 (mean 36·3).

Detection of Adulteration.—Cacao butter being a valuable fat is liable to adulteration and substitution. One of the commonest substitutes (such

* 0·883 at 60/15·5 (Tate and Pooley); 0·858 at 99/15·5; 0·973 at 25/25.

† Mostly 32·5°-33·5°. H. Fincke (*J.S.C.I.*, 1925, 44, B. 640, B. 813). Cf. T. Sabalitschka (*J.S.C.I.*, 1926, 45, 20 B).

‡ Knapp considers that these figures must be accepted with extreme reserve; they are entirely outside his experience.

substitutes are sometimes known as " Chocolate fats " but this name would appear to be most undesirable. " Chocolate fat substitute " or " Cacao butter substitute " would appear to be unobjectionable) is coconut oil, or coconut stearine or substitutes of the same class (*J.S.C.I.*, 1902, 21, 55. *Analyst*, 1908, 33, 123). The detection of these present no difficulty, as a determination of the Reichert and Polenske values will at once show their presence (cf., also Strube, *Analyst*, 1908, 33, 188, 10; Wauters, *Analyst*, 1911, 36, 275). Other substances that have been used are tallow, lard, stearic acid, beeswax, hard paraffin and other vegetable oils. A likely substance is the kernel oil obtained from a species of *Astrocaryum* which is described on page 354 (cf. Bolton and Hewer, *Analyst*, 1917, 42, 35). Liquid vegetable oils would be readily recognised by the increase in the iodine value; solid vegetable fats will be dealt with below. Beeswax and hard paraffin (unlikely additions at the present time) would be indicated by a low saponification value and a large amount of unsaponifiable matter. the former will increase the acid value of the sample as also will the addition of stearic acid. The hydrogenated oils may be used but this requires some care (cf. Myddleton and Barry, page 153).

The presence of tallow may be detected by the method of Björklund which is carried out as follows:

Three grm. of the fat are shaken in a well-corked test-tube with twice their weight of ether at 18°. If wax be present, the solution will be turbid and will not become clear even on warming. Genuine cacao butter will dissolve to a clear solution. If a clear solution is obtained, the tube is immersed in water at 0°, and the number of minutes noted which elapse before the liquid becomes turbid, also the temperature at which the solution again becomes clear on warming. The following are Björklund's observations:

TABLE CXLIX.—BJÖRKLUND'S TEST FOR TALLOW IN CACAO BUTTER

	Turbidity at 0° after Minutes.	Clear Solution at degrees.
Pure cacao butter	10–15	19–20
Cacao butter, 5 per cent. beef tallow . .	8	22
Cacao butter, 10 per cent. beef tallow . .	7	25

Lewkowitsch (*J.S.C.I.*, 1899, 18, 557) found that cacao butter containing as much as 10 per cent. of tallow will dissolve in 2 parts of ether at 18, although requiring a little longer than the genuine butter does, and that the chief indication to be relied upon is not so much the time required for crystallisation to begin, as this varies with different samples of cacao butter, but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. With genuine samples, distinct tufts of crystals appear at the bottom and sides of the tube, whereas 5 per cent. and more of tallow are recognised by flocks separating from the chilled solution.

The presence of tallow may possibly be confirmed by the isolation of cholesterol from the unsaponifiable matter which remark will also apply to lard (the latter will probably raise the iodine value unless lard stearine be

used when the ether crystallisation method may be useful) but the recent work of Steuart (see page 127) must not be overlooked in this direction; further work on the subject is necessary.

The presence of many of the solid vegetable fats (frequently sold as "green butters," page 282) is sometimes a difficulty. The most common additions are Bassia tallow (see page 278) and Borneo tallow (page 282). The former is distinguished from cacao butter by the considerably higher iodine value, but the properties of the latter are so similar to those of cacao butter that at one time it was (and may be now) impossible to detect quite large admixtures.

The question of the addition of Borneo tallow (frequently but erroneously called Illipé butter) has been studied at length by Tate and Pooley (*Analyst*, 1921, 46, 229). These authors, although realising that any one characteristic taken by itself is of no value for the detection of admixture, suggested that a series of suitable constants, determined in a standard manner should be multiplied together so that the differences due to the two oils should thereby be intensified. The characteristics used for the purpose were the gravity at 60°, the gravity at 99°, the viscosity, the melting-point, the melting-point of the free fatty acids and the reciprocal of the iodine value.

These factors were observed for 14 samples of commercial cacao butter and for 16 samples of Borneo tallow (Illipé butter) with results as given in the following table:

TABLE CL.—COMPARISON OF CACAO BUTTER WITH ILLIPÉ BUTTER

	Cacao Butter.			Illipé Butter.		
	Max.	Min.	Average.	Max.	Min.	Average.
Specific gravity at 60°	0·8830	0·8823	0·8825	0·8840	0·8820	0·8826
" " 99°	0·8581	0·8572	0·8575	0·8589	0·8569	0·8577
Viscosity	101·3	99·0	99·9	105·7	100·7	103·7
Melting-point, °C.	31·2	30·2	30·5	35·8	31·0	33·2
Iodine value	40·1	34·6	39·8	33·4	27·4	31·5
Fatty acids, M.Pt., °C.	49·2	47·7	49·4	54·1	52·0	52·8
Refraction, n_D^{40}	1·4570	1·4568	1·4569	1·4573	1·4561	1·4568

When these results are multiplied out in the suggested manner the following results are obtained:

Cacao butter: 3347, 3266, 3252, 5194, 3191, 3169, 3149, 3130, 3123, 2972, 2839.

Illipé butter: 4771, 4714, 4652, 4535, 4503, 4487, 4463, 4397, 4279, 4112, 3901, 3890.

If the average of these two series be obtained it is found that cacao butter gives a value of 3150, whilst Borneo tallow gives 4403. The authors give a table showing that they have obtained excellent results by this method, but at present no great support has been given to it by other workers; further work is desirable.

Tate and Pooley also suggested a "short factor" which consisted of the melting-point of the fatty acids and the reciprocal of the iodine value whence they obtained 4166 for cacao butter and 5615 for Borneo tallow; they recommend, however, the "long factor" wherever possible.

A test for differentiating between cacao butter and " green butter " has been devised by Halphen (*Analyst*, 1908, 33, 468) which may be carried out as follows:

One grm. of the absolutely clear filtered fat is dissolved in 2 c.c. of carbon tetrachloride; to 2 c.c. of this mixture is added a solution of bromine in carbon tetrachloride (made by adding bromine to an equal volume of carbon tetrachloride) drop by drop until the colour of the bromine is just permanent; to the mixture are added 3 c.c. of petroleum (sp. gr., 0·700), and the tube stoppered and allowed to stand twenty-four hours at ordinary room temperature. Under these circumstances a solution of cacao butter remains perfectly clear whilst " green butters " give a flocculent precipitate which will detect 5 per cent. of " green butter."

This test was studied by Revis and Bolton (*Analyst*, 1913, 38, 201), who found that it was not satisfactory as several " green butters " gave practically no precipitate at all. They were able to modify the test so that it became a test for cacao butter the presence of 10 per cent., of which in " green butter " could be detected. They carry out their test as follows :

One grm. of the clear filtered fat is dissolved in 2 c.c. of a mixture of equal parts of carbon tetrachloride and petroleum ether (distilling below 40°), and 2 c.c. of this solution are placed in a test-tube about 6 inches long and $\frac{1}{4}$ inch in diameter. This tube is cooled in water, and the solution of bromine in carbon tetrachloride (see above) added drop by drop, with constant shaking, until the colour of the bromine is permanent. The greatest care must be taken that only one drop in excess is allowed. The tube is then corked and allowed to stand. If, after the expiration of fifteen minutes, the solution is perfectly clear, cacao butter is not present, or there is less than 10 per cent. If the solution shows any turbidity, the presence of cacao butter is indicated, except in the case of one—somewhat rare—cacao butter substitute obtained from a species of Gutta nut. This one exception, however, does not give quite the same turbidity as cacao butter, and can easily be distinguished as described below.

The method can be made roughly quantitative by making mixtures of cacao butter and some solid fat of low iodine value (such as coconut oil or coconut " stearine " if an actual " green butter " is not to hand), and comparing the turbidities produced by these mixtures and the sample under examination.

After the turbidity has been compared, 2 c.c. of petroleum ether are added to the tubes, which, after mixing by inversion, are allowed to stand all night, when the cacao butter turbidity settles out as a fine canary-coloured precipitate, easily distinguished from the slight flocculent precipitate which " green butters " under these circumstances usually throw down. It is to be also noted that cacao butter is completely soluble in the carbon tetrachloride-petroleum-ether mixture in the strength given above, whereas " green butters " usually become turbid almost immediately, and on standing for two hours usually throw down a considerable precipitate. Care must therefore be taken that the solution used for the test is quite clear.

The fat mentioned above, which might possibly be mistaken for cacao butter, may be distinguished from true cacao butter as follows : The solution of the fat, after treatment with the bromine, is allowed to stand for fifteen minutes, and the turbidity is then carefully examined by transmitted light. The turbidity due to cacao butter is absolutely non-flocculent, and any appearance of flocculent particles is characteristic of this other fat. If now to the brominated solution are added 2 c.c. of petroleum (fraction of

motor spirit distilling between 90° and 100° C.) and the whole mixed, any turbidity due to cacao butter entirely dissolves, whilst the turbidity due to this other fat remains quite insoluble.

By this means 5 per cent. of this fat may be detected in admixture with 95 per cent. of cacao butter or "green butter." More than 10 per cent. of this fat produces such a heavy flocculent precipitate that it could not possibly be mistaken.

The following method for the detection of kernel oils has been proposed by W. F. Baughman (*J.A.O.A.C.*, 1925, 8, 703) :

> Saponify 5 grms. of the sample with 10 c.c. of the alcoholic potash solution (25 grms. of potassium hydroxide in 200 c.c. industrial spirit). Evaporate the alcohol on the water-bath. Add 5 c.c. of water and evaporate to remove last trace of alcohol. Dissolve the soap in 100 c.c. of water; cool to room temperature; and add while stirring, 100 c.c. of the saturated common salt solution. Allow to stand fifteen minutes and during this period stir several times. Remove the separated soap by filtration, using a Buchner funnel. To 100 c.c. of the filtrate add, while stirring, 100 c.c. of the saturated salt solution and allow to stand fifteen minutes. Only a slight precipitate should appear. Filter, and slightly acidify the filtrate with hydrochloric acid. Run a blank on a sample of pure cacao butter at the same time. If the sample consists of pure cacao butter or fat from milk chocolate, the solution will remain clear or almost clear when acidified. If coconut or palm-kernel oil is present, the solution will become turbid or milky.

Grimme (*Analyst*, 1914, 39, 216, 434) found a cacao butter substitute originating in Amsterdam and known as "Elite" (trade-mark a swan) which had the following characteristics :

Sp. gr. at 65°, 0·8800 and 0·8828; at 15°, 0·9150 and 0·9178; melting-point, 30° and 30·4°; solidification-point, 28° and 28·1°; refractive index at 40°, 1·4559 and 1·4558; acid value, 2·1 and 1·95; saponification value, 198·4 and 198·0; iodine value, 38·3 and 38·14; Reichert-Meissl value, 0·82 and 0·94; and Polenske value, 1·5 and 1·52. *Fatty acids.*—Melting-point, 46° to 48° and 46° to 47·5°; solidification-point, 45° and 44·9°; refractive index at 40°, 1·4552 and 1·4554; neutralisation value, 207·0 and 206·3; iodine value, 38·82 and 38·53, and mean molecular weight, 271·0 and 272·1. The only notable differences between these results and those given by pure cacao butter were the lower melting-point of the fatty acids (which were also brownish-yellow instead of pale yellow or white) and the Polenske values. The critical temperature of solution in glacial acetic acid (35° as compared with 65° to 69° for genuine cacao butter) indicated the presence of a foreign glyceride. By fractional crystallisation of the fats from a mixture of anhydrous ether and alcohol (3 : 1) at 10° C., the adulterated fats yielded first fractions which were semi-solid and second fractions melting at 39·7° C. and 40° C., whilst four samples of pure cacao butter gave first fractions melting at 46° to 52° C., and second fractions melting at 50° to 57·4° C.

Bellier has proposed a reaction for cacao butter which is given on mixing together equal volumes of the fat, nitric acid S.G. 1·38 and a saturated solution of resorcinol in benzene. N. Béard-Clemencet (*J.S.C.I.*, 1924, 43, 525B) has found that the minimum percentage of cacao butter which, diluted with a neutral medium such as vaseline, will give a positive reaction is 9 to 10, so that pure cacao butter diluted in this way to 10 per cent. should give a positive reaction. Other oils such as tallow, coconut oil and hydrogenated

arachis also give a somewhat similar reaction so that the test has at the best a somewhat limited application.

Miscibility tests have a considerable amount of value and much work has been done along these lines. The American Association of Official Agricultural Chemists (cf. *Analyst*, 1923, 48, 224) suggest the Valenta test carried out in a particular way (see Valenta test, page 89) and propose further a test with a reagent consisting of equal parts of acetone and carbon tetrachloride carried out in the following way :

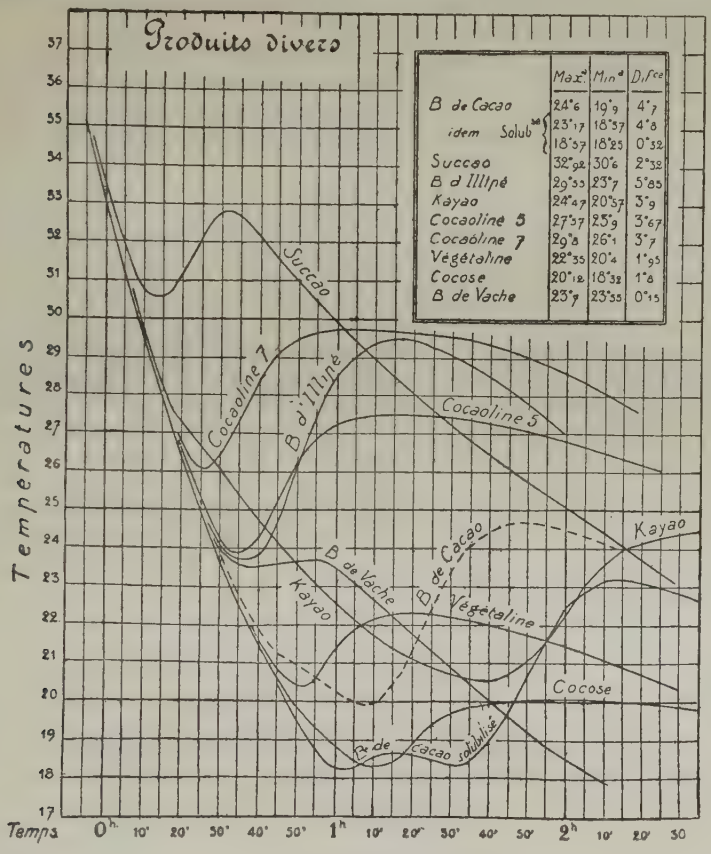

FIG. 7.—Cacao Butter Curve

[*Reproduced by permission of The Analyst*

" Dissolve 5 c.c. of the warm fat, which has been previously filtered through dry filter paper in an oven at about 110° to remove traces of moisture, in 5 c.c. of the acetone and carbon tetrachloride reagent in a test-tube. Allow the solution to stand in ice water for 20–30 minutes. Run a blank on a sample of pure cacao butter at the same time. If hydrogenated oil, tallow, oleostearine or paraffin wax is present, a white flocculent precipitate will soon appear. If the water is cold enough, cacao butter may solidify. If a precipitate is formed, remove the sample from the ice water and allow it to remain at room temperature for a time. Solidified cacao butter will soon melt and go into solution, but, if the precipitate is due to any of the above-mentioned possible adulterants, a much longer time will be required for it to go into solution."

Koehler (*Analyst*, 1924, 49, 237) uses ethyl acetoacetate for the process. The method he uses is to run the ester from a burette into a 20 per cent. solution of the cacao butter in chloroform at a temperature of 15°–20°, until the appearance of a turbidity which is not increased by a further drop (an end point quite easily recognised). The number of c.c. of ester required by 2 c.c. of the 20 per cent. solution is called " the turbidity index," and is remarkably constant for pure cacao butters, but is increased by an adulterant. In the case of samples grossly adulterated the ester may precipitate the adulterant; in such cases the solution is diluted with a 20 per cent. solution of a pure cacao butter.

The principle of miscibility curves was first proposed by Louise and Sauvage (*Analyst*, 1907, 32, 365) and is described on page 94. The principle has been adapted to cacao butter by Marange (*J.S.C.I.*, 1923, 42, 840A) and by Rosset, Morange and Vinter (*Analyst*, 1924, 49, 91), who use aniline-alcohol mixtures.

M. Pichard (*Analyst*, 1923, 48, 556) has done a considerable amount of work on the form of the curve obtained when cacao butter is allowed to cool under standard conditions, the temperature readings taken at intervals of five minutes and plotted as ordinates whilst the times are plotted as abscissæ. In the case of pure cacao butters the curves representing the variation of the temperature with the time are similar and almost superposable, no matter what the origin of the cacao beans, their degree of maturity, or the extent of the torrefaction or pressure applied in extracting the butter. For other fatty materials capable of fraudulent employment in the manufacture of chocolates, or coatings, or of direct admixture with cacao butter without sensibly modifying the appearance or the chemical and physical constants of the butter, the curves obtained differ widely, not only from that of cacao butter, but also among themselves. For mixtures of cacao butter with foreign fats, the curves are not exactly intermediate to those given by the separate constituents, but either lie outside of these curves or follow quite different courses.

The following table shows the results obtained with cacao butters of different origin and modes of preparation. In each case the maximum represents the rise of temperature following the incipient solidification at the minimum :

TABLE CLI.—MISCIBILITY TESTS OF CACAO BUTTER

	Maximum. °C.	Minimum. °C.	Difference. °C.
Sanchez	23·75	19·4	4·35
Arriba	24·55	19·925	4·625
Puerto Cabello . .	24·475	19·775	4·7
Martinique . . .	23·62	19·325	4·3
Lome	24·475	19·9	4·575
Gaudeloupe . . .	24·5	19·525	4·975
Bahia	23·4	18·5	4·9
Congo	24·3	20·3	4·5
Cameroons . . .	24·8	20·15	4·65
Caraque	25·0	20·00	5·00
Haiti	24·25	19·85	4·4

The curves of the fat from "solubilised" cocoa differ materially in form from those of the fats of the same cocoas which have not been thus treated. After reaching the first minimum they rise slightly, then fall, and then rise to a final maximum. The difference between the second maximum and minimum, however, agrees with that of a normal cacao butter. For example, the following results were obtained with the fats from three samples of Dutch cocoa :

	Maximum. °C.	Minimum. °C.	Difference. °C.
Franken	19·35	19·2	0·15
	23·1	18·8	4·3
Korf	19·3	18·96	0·35
	23·4	18·9	4·5
Boon	18·575	18·25	0·32
	23·175	18·325	4·85

In the case of mixtures of illipé butter with cacao butter the minimum point is always higher than that of pure cacao butter, and the curves are above those of pure products. For example, the following results were obtained with mixtures :

TABLE CLII.—MISCIBILITY TESTS ON MIXTURES OF ILLIPÉ BUTTER WITH CACAO BUTTER

	Maximum. °C.	Minimum. °C.	Difference. °C.
Cacao butter	25·675	19·95	4·725
Illipé butter	29·5	23·7	5·8
Cacao butter 20%, illipé butter 80% .	25·878	20·6	5·275
" " 66·6% " " 33·3% .	26·5	20·9	5·6
" " 50% " " 50% .	27·45	21·2	6·25
" " 33·3% " " 66·6% .	28·55	21·8	6·75
" " 25% " " 75% .	28·925	21·05	7·875

The figures given by karité butter and the form of its curve are quite different from those of cacao butter, e.g., maximum, 25·00°; minimum, 19·85°; and difference, 5·15°. The solidification begins at 25·6°, and the rise from the minimum to the maximum is so abrupt that the curve forms an acute angle.

A somewhat novel method of examination is proposed by Andoyer (*J.S.C.I.*, 1924, 43, 570B), who determines the calorific value of the fat. The following values were obtained for the dry filtered fats in a Mahler bomb calorimeter : Cacao butter 9070–9090, oleomargarine 9215–9245, cotton-seed oil 9670–9695, rape oil 9600–9620, butter fat 9355–9395 cals. This method has, of course, the disadvantage of requiring specialised

apparatus, whilst, of course, it is quite possible that the usual cacao butter substitutes may give similar figures to cacao butter itself.

Fat from other Species of Theobroma. — The fat from *T. grandifolia* (Cupa seeds) has been examined by Bray and Islip (*Analyst*, 1921, 46, 325) and by Bolton and Hewer (*Analyst*, 1922, 47, 282) and that from *T. bicolor* (Lupu seeds) has been examined by the latter authors. Both these fats are somewhat similar to cacao butter but are softer and without odour. The characteristics observed for these fats by the authors named are given in the following table :

TABLE CLIII.—EXAMINATION OF FAT FROM THEOBROMA GRANDIFOLIA

Characteristics.	Cupu.		Lupu.
	Bray and Inslip.	Bolton and Hewer.	Bolton and Hewer.
Melting-point °C.	32·0	45·5	42·1
Titre °C.	48·1	..	..
Acid value	44·0	44·0	22·0
Saponification value	187·8	189·2	189·0
Iodine value	44·8	44·3	44·4
Unsap. matter per cent.	0·91	..	0·9
Reichert value	0·1	..	..
Polenske value	0·1	..	..
n_D^{40}	1·4560	1·4563	1·4565

CHAPTER XXII

PALM OIL

Palm oil is obtained from the fleshy pericarp of the fruit of *Elæis guineensis*. It must not be confused with palm-kernel oil which is obtained from the kernels of the same fruit and which is quite different in properties and composition.

" The oil palm is indigenous to West Africa, and occurs in the coast belt almost continuously from the French colony of Senegal to the Portuguese colony of Angola, or approximately from 16° N. lat. to 10° S. lat., but is found in greatest abundance from Sierra Leone to the Cameroons. Inland it penetrates to great distances, and is found as far in the interior as the great lakes and less frequently right across the continent and in the islands of Zanzibar and Pemba. Dense forests of oil palms are, however, only found in the coastal region, and in West Africa it does not occur thickly much beyond 200 miles from the coast. The commercial supplies of palm oil are obtained mainly from Southern Nigeria, Sierra Leone, the Gold Coast Colony, Dahomey, the French Congo, the Cameroons, Togoland and Angola, whilst there have been in recent years small exports of palm kernels from the island of Pemba on the east coast and of palm oil from German East Africa, where oil palms occur in abundance along the shores of Lake Tanganyika, but owing to lack of transport facilities are not much worked for export "—*Bulletin of the Imperial Institute.*

The palm also occurs in Brazil and along the Amazon and these countries are not unlikely to become sources of supply. The Brazilian palm, however, although yielding a fruit indistinguishable in appearance and structure from that of the tree which grows in Africa contains less fatty matter and fatty matter of a distinctly different constitution from that of the latter (Bolton and Hewer, *Analyst*, 1917, 42, 35). The figures for that from the Brazilian palm are given in the table.

The tree has been cultivated in various districts in the East Indies both in Dutch and British Colonies; this has been going on for some years. It was introduced into the Dutch Indies in 1848 but did not receive much attention until about 1910. Since this time considerable progress has been made as is shown by the fact that from January 1918 to January 1922 the area planted with oil palms increased from 8500 acres to 28,000 acres. In Malay in 1923 about 3000 acres had been planted of which about 500 were actually producing oil.

" The full-grown oil palm may attain a height of about sixty feet, and consists of a stem covered throughout its length with the bases of dead leaves, and bearing at the apex a crown of large, pinnate leaves, each of which may be fifteen feet in length with leaflets two or three feet long. The tree is very slow growing, and from measurements made in the Agege district of Southern Nigeria reaches a height of six to nine inches in three years, twelve to eighteen inches in four or five years, eight feet in ten years, and thirteen to fourteen feet in fifteen years, and it is estimated that it attains its full height of sixty feet in about one hundred and twenty years. The fruits are borne in large bunches termed " heads " or " hands," which are small and numerous when the tree first begins to bear (this varies from the fourth to the eighth

year according to climatic conditions, etc.), but decrease in number and increase in size in the next few years; thus in Southern Nigeria, according to Thomson, as many as thirty ' heads ' may be formed at first, decreasing to anything between two and twelve as the tree ages. The fruits are usually from one to one and a half inches in length, and three-quarters to one inch in diameter and are roughly egg-shaped, the narrower end being the apex. The colour and size depend on the variety of oil palm, but usually the fruits are reddish-brown or orange in tint. The fruit is botanically a drupe, and consists of three well-marked portions. Outside is a layer varying in thickness and composed of a soft fibrous pulp (pericarp), carrying from 55 to 65 per cent. of an orange-coloured, semi-solid fat, which when extracted constitutes the palm oil of commerce. Inside this pulp is the palm nut (endocarp), consisting of a hard woody shell, which may vary considerably in thickness, enclosing usually a single palm kernel, though sometimes two or even three are present; the kernel is the second useful product of the palm fruit; it is dark reddish-brown or almost black externally, and internally consists of a rather hard, white ' flesh ' loaded with oil, which when extracted constitutes the ' palm-kernel oil ' of commerce

" The tree will apparently grow on most soils which are capable of holding a fair quantity of moisture, but it is only on rich moist soils and in districts having a fairly high rainfall (50 to 70 inches on the average) that it gives good yields of fruit. Thus in a recent article on the oil palm in Southern Nigeria (*Southern Nigeria Gazette*, 1908, No. 10, Suppl.) it is pointed out that the common variety is confined to the moist belts of country, and is most plentiful on the native farms and in the evergreen forests of the Niger delta and some of the littoral districts of the Eastern Province, where a heavy annual rainfall is experienced. In the hinterland of Southern Nigeria, where the rainfall is deficient, the distribution of the tree follows the evergreen

TABLE CLIV.—CHARACTERISTICS OF PALM OIL

Authority.	S.G. 15°.	M.Pt. °C.	Sap. Value.	Iodine Value.	n_D^{40}.	Titre. °C.	M.Pt. Acids. °C.	I.V. Acids.
Mitchell . .	0·921–0·925	27–43	200–205	53–58	..	35·8–47·6	48–50	49–59
Fryer & Weston.	0·921–0·924	35–43	200–203	52–56	1·4531–1·4559	36–45	..	..
Tipler . . .	..	42–50	..	52–58	..	40–44·9	..	49–58·3
Bolton & Hewer*	..	30	197	78–88	1·4583–1·4603	..	..	..
Bolton & Hewer†	..	38	200·6	55	1·4548	..	..	..
Hébert . . .	..	42–45	196–201	43·8–55·6	..	..	44–48	.. ..

* Brazilian. † African.

belts of the forests skirting the large streams. It is conspicuously absent from the impoverished grass-covered soils on which the fan-palm typically occurs, indicating that a dry climate and poor soil do not suit it."—*Bulletin, Imperial Institute.*

Until quite recent times palm oil was obtained by more or less crude methods by the natives, and the resulting oil was frequently of inferior quality, being of high rancidity and containing numerous impurities. The fruits are usually gathered just as they become ripe by men who climb the trees and allow the bunches to fall to the ground as they are cut off. The bunches are collected and placed in a pit lined with leaves, moistened with water, covered with more leaves and allowed to stand for a period varying from one to many weeks. During this time the fleshy pericarp of the fruit (which is the source of the palm oil), which is at first quite firm, becomes softened so that the palm kernels (the source of palm-kernel oil) may be the more readily removed. This is brought about by pounding up the softened fruits with wooden staves after which the oil is expressed from the pulped mass by means of crude bag presses or allowed to drain away by standing under suitable conditions. The kernels are then picked out by hand and the pulp mixed with water, the mixture boiled in large iron vessels, and then the oil which rises to the top is removed by suitable implements. The residue from this treatment is again expressed in a bag press when a further quantity of oil is produced.

The following description of the process formerly in use in the Gold Coast is due to the Inspector of Agriculture for West Africa and is quoted in the *Bull., Imp. Inst.*, 1909, 7, 385 :

" After the bunches have been allowed to stand for a few days the fruits are chopped out and piled in heaps on a paved or cemented basin having a diameter of about eight feet and a slightly depressed rim about two feet in width running completely round, and in one place a small well connected with the bottom of the basin by a wooden tube. The heap of fruit is covered with leaves and left for five or six days, during which period fermentation takes place and the mass becomes hot. At the end of that time the heap is uncovered, and five or six people proceed to pound the mass with poles for several hours. After this treatment the mass is again covered up, left for two days, and the pounding again repeated, followed by a further fermentation for two days and a further pounding. From the time of the first pounding oil begins to flow through the tube into the well, and as the latter fills up it is emptied by means of small calabashes. When no more oil flows the nuts are picked out of the mass of pulp, and the latter is collected, boiled in water in order to cause a little more oil to separate, and is finally squeezed in a primitive press. The nuts are dried in the sun so that the kernel may shrink and be readily detachable from the shell. The nuts are cracked singly by hand, each nut being placed on a stone and struck with a second stone. It is stated that an industrious native can prepare about four pounds of kernels per day in this way, the shells being afterwards picked by hand."

These crude wasteful native methods are in course of being abandoned. In the Nigerian Court of the Wembley Exhibition 1924, an oil mill was exhibited by Messrs Nigerian Products Limited, 21 Dale Street, Liverpool—a mill which was destined for use later in West Africa. The following description of the plant and its method of operation are taken, by permission, from a pamphlet issued by the company :

" The fruit is fed by means of a creeper or conveyor from the buying store to an elevator discharging into a receiving hopper, which feeds two

enclosed digesters. (In the Exhibition plant the fruit was fed by hand to the elevator, thence direct into the digester, only one of which was shown, the receiving hopper also not being shown.) Each digester has a capacity of 30 cwts. of fruit, and is fitted with vertical shaft and agitators which stir the contents, whilst steam is admitted under pressure.

After 15 to 30 minutes steaming, the fruit is discharged into a creeper feeding three centrifugal extractors. (In the Exhibition plant only one centrifugal was shown, and the creeper was omitted, the fruit being fed to the centrifugal by a sliding shute.) The centrifugal is fitted with a removable basket having a capacity of about 5 cwts. The charge is centrifuged for about ten minutes, the oil being thrown through the perforated basket and discharged by a pipe in the outer casing of the centrifugal to a ground tank; from this it is pumped to settling tanks and thence to a storage tank, from which the oil is drawn off into casks or drums for shipment. (The settling and storage tanks were not exhibited.) The extraction of the oil is assisted by the injection of steam into the centrifugal whilst running. In the main plant three centrifugals are used, with an extra basket to expedite working.

" After centrifuging, the basket containing the residue of nuts and fibre is lifted by means of chain blocks and carried by an overhead runway to a hopper feeding a rotary dryer. The dryer is heated by the exhaust gases from the boiler, the products of combustion being drawn through by means of an induction fan. (For Exhibition purposes a gas-fired boiler was used, but in actual practice in West Africa the exhaust gases from an ordinary steam furnace are used to heat the dryer, the fuel being shell and fibre, the waste products of the process.)

" The interior of the dryer is fitted with angle baffle plates which lift the ' mat ' of nuts and fibre, the dryer being rotated by means of an external toothed wheel, and the induced hot gases drive off the moisture; the dryer is slightly inclined to allow the nuts and fibre to pass slowly through the cylinder, and after about 20 minutes the mass is discharged at the opposite end into an elevator feeding a rotary screen, where the nuts and fibre, now thoroughly dry, are separated, the fibre falling through the mesh, and the nuts travelling through the screen, are discharged into the boot of an elevator feeding two nut-cracking machines (Miller's patent).

" The nut-crackers are placed side by side, and one or both may be used as required; they are driven through a counter-shaft at about 1000 revolutions per minute.

" After cracking, the kernels and broken shell fall on to a shaker screen which recovers any uncracked nuts, but allows the kernels and shell to fall through the mesh into a brine bath; the density of the brine floats the kernels, but allows the shell to sink. The bottom of this tank is filled with a spiral conveyor propelling the shell to the end, whence it is elevated to a receiving hopper feeding a centrifugal machine in which the brine is extracted and returned to the brine tank; the shell contained in a removable basket, is taken to the boiler furnace by means of an overhead runway. The kernels are skimmed off the surface by means of wire baskets and, after standing for a few minutes on a drip tray to drain, are fed into a centrifugal machine and treated in a similar manner to the shell. They are now dry and ready for bagging.

" In the main plant for West Africa separate centrifugals are used for the shell and kernels, but at the Exhibition, owing to restricted space, one served the dual purpose.

" The plant has been designed with a view to labour-saving, and is practi-

cally automatic from start to finish. The complete mill is capable of treating 20 to 30 tons of palm fruit per day of 10 hours."

In this process fermentation is not allowed to take place so that the oil produced is of much higher quality than that usually prepared by the natives.

The inferior oils may be refined for edible purposes according to Lauro and Dickhart (*J.S.C.I.*, 1922, 41, 432A) by means of caustic soda to remove the free fatty acid, the colour being subsequently removed by exposing the oil to light in shallow aluminium dishes for several days at 105°–110° and subsequently deodorised by means of live steam.

The fruits are, generally speaking, of small size, being from 1 to 2 inches in length, about 1 inch in diameter, and weighing from 3 to 14 grms. each, the average weight being about 7 grms. The proportion of pulp varies considerably, being in some cases as low as 25 per cent., whilst other varieties yield as much as 75 per cent. The average figures are about one-third pulp and two-thirds nuts. The pulp contains from 55–75 per cent. of oil. Palm kernels and palm-kernel oil are dealt with on page 343.

Composition.—The acids of palm oil consist essentially of palmitic and oleic. About 1 per cent. of stearic acid appears to be present together with a small proportion of linolic acid (Nördlinger, *J.S.C.I.*, 1892, 11, 445). No recent work has been done on this subject. Such work is somewhat desirable, more particularly a comparison of the composition of palm oils from various sources.

Properties.—Palm oil is a solid fat of a consistency varying from that of soft paraffin to that of tallow. This consistency depends largely on the mode of preparation, the oil obtained from the fresh fruit being soft in texture and having an agreeable odour. The colour is also very variable, ranging as it does from a comparatively light-yellow to a deep orange-red, in some cases passing almost to black with impurities. The oil used for edible purposes is, of course, neutral oil having little colour and odour. The purest oil has a characteristic pleasant odour but this, in the case of impure and rancid oils, is frequently most objectionable. Commercial oils are usually highly rancid and contain large quantities of free fatty acids. The acid value of some commercial oils is over 100, whilst in extreme cases of very old oils the hydrolysis may go to completion and the oil consist entirely of free fatty acids.

The oil is bleached quite readily on exposure to air, but on the commercial scale the process is usually carried out by means of a mixture of dichromate and hydrochloric acid at a moderate temperature, an alternative method being the blowing in of air at a temperature of about 100° and raising the temperature according to the requirements of each particular oil.

Palm oil is not often adulterated with other fats and its examination is usually confined to a determination of acidity (frequently expressed as per cent. of palmitic acid), water and solid impurities, the latter of which are not infrequently added by the natives as adulterants. The commercial valuation of an oil depends upon the amount of sand and water, which together should not exceed 2 per cent.; for any excess over this, an allowance is usually made by the seller. Hupfeld (*J.S.C.I.*, 1914, 33, 146) has suggested the following limits for edible fats : acid value, 16; dirt, 0·5 per cent.; water, 0·5 per cent.

The Reichert value of palm oil has been given by various observers as 0·7 to 1·9, but these high figures are probably only correct in the case of rancid oil. Oils of good quality will probably have a negligible Reichert value.

The Crampton-Simons colour reaction for palm oil (*Analyst*, 1905, 30, 250) depends upon the formation of a green colour when the oil is treated with acetic anhydride containing a trace of sulphuric acid. It has been shown, however, by Gill (*Analyst*, 1917, 42, 216) that this reaction is really due to the presence of carotin and that it is given by any fat or oil such as butter, sesamé, etc., which contains this substance.

A large number of varieties of palm have been studied by various workers in recent years. Bolton and Hewer, in addition to their study of the Brazilian type of *Elæis guineensis*, the results of which are given in the table on page 316, have studied those growing in Brazil and have obtained interesting results. Some of these will be found under Grou-grou oil, Tucan palm oil, Cokerite palm oil, Babassu oil, palm-kernel oil and coumou oil. The results given below were obtained on the fruits of *Cocos syagrus*. The authors state that "two distinct types have been examined, the more common being a blunt form, which consists of a hard shell sparsely covered with fibre, enclosing a tough white kernel covered by a brown, woody skin. The pointed kernels are similar in every way except shape. The structure of both the long and blunt kernels is strikingly characteristic in that they have three points of attachment, close together in the former, and widely apart in the latter.

Although the proportion of oil in the two types is very different (the blunt containing the greater quantity) in their nature the two are practically identical, and it is curious to note that the author's analytical figures bear a striking resemblance to those given by Bray and Elliott for *Maximiliana regia*, though clearly the nuts are not the same.

The results obtained are set out in the following table :

TABLE CLV.—COMPARISON OF BLUNT AND POINTED PALM FRUITS (*Cocos syagus*)

	Blunt Fruits.	Pointed Fruits.
Weight of 100 fruits or seeds in grms.	1100	600
Per cent. of kernel	40	41
Kernel : Oil content per cent.	32·1	23·0
Analytical figures for Oil.		
Melting-point °C., incipient fusion	23	23
,, complete fusion	29	28·7
Solidifying-point °C.	26·8	..
Saponification value	252·2	..
Refractive index Zeiss at 40°	37·4	36·2
Iodine value	12·5	13·4
Free fatty acid per cent.	3·2	2·97
Unsaponifiable matter	..	..

The oil is obviously similar in type to the other kernel oils.

A new species of oil palm (*E. poissonnii*) has been described by Fauchère (*J.S.C.I.*, 1918, 37, 741A). It is stated by this writer that the fruit of this plant is peculiar in that it is enclosed in a sort of fleshy sheath formed by the development of six staminodes contained in the female flower, which, in the varieties of *Elæis* hitherto described, are always atrophied. The fruit weighs from 10 to 20 grms. The following table gives comparisons of the new species (of which two varieties are to be distinguished—var. *tenera*

and var. *dura*) with the var. *Lisombe* or *Elæis nigrescens* (the best form of oil palm known at present):

	Tenera per cent.	Dura per cent.	Lisombe per cent.
Oily pulp	76	44	61·5
Nuts	24	56	38·5
Oil yield of the pulp	70·25	58·6	63·15
Oil yield of the whole fruit	53·50	55·8	38·35

The following figures were obtained from an examination of ten fruits of each of the chief varieties of *Elæis* in the Cameroons:

	Weight in Grms.			
	Fruit.	Pulp.	Kernel.	Oil.
Dibope	123·0	51·5	23·0	27·0
Lisombe	121·5	76·5	20·5	47·0
Dura	171·0	74·2	18·1	44·0
Tenera	168·5	128·3	19·4	90·0

The pulp oil of *E. melanococca*, Gærtn., has been described by the Imperial Institute (*Analyst*, 1920, 45, 48). This is stated to be similar in character to *E. guineensis* but smaller in size and to be common in Columbia where it is known as the Noli Palm. The fruits are dry, of orange-yellow or greyish colour, from 0·8 to 1 inch in length, and from 0·5 to 0·8 inch in diameter; average weight of a single fruit, 2·5 grms. The shells of the nuts are very hard, and about 0·1 inch in thickness. The fruits consist of pericarp 16 per cent., shell 62 per cent., and kernel 22 per cent.

The pericarp of the sound fruits contained 8·1 per cent. of moisture and 29 per cent. of oil, equivalent to 31·5 per cent. of oil from the dry pericarp. The yield of oil from the entire fruit is therefore only 4·6 per cent. The oil itself is an orange-yellow liquid containing a fairly high proportion of stearine. It is much more liquid and paler in colour than commercial palm oil from West Africa, but is similar in taste and smell.

The following results were obtained:

TABLE CLVI.—CHARACTERISTICS OF OIL FROM ELÆIS MELANOCOCCA

	Pericarp Oil from Noli Palm Fruits.
Sp. gr. at 100°/15° C.	0·8636
Solidifying-point of fatty acids	33·6° C.
Acid value	29·7
Saponification value	199
Iodine value per cent.	83·5
Unsaponifiable matter per cent.	0·7
Volatile acids, soluble	0·7
,, ,, insoluble	0·5

A large amount of information concerning palm oil and palm oil products is contained in back volumes of the *Bulletin of the Imperial Institute*. (Cf. *Analyst*, 1910, 35, 166; *J.S.C.I.*, 1910, 29, 287; 1913, 32, 797; 1917, 36, 1017.) For further information the following papers may be consulted:

" The Yield and Description of Oil Palms in the Tanganyika District." E. Zimmermann. *J.S.C.I.*, 1911, 30, 1265.

" The Catalytic Bleaching of Palm Oil." Sastry. *J.S.C.I.*, 1916, 35, 126.

" The Composition of ' Wine ' Obtained from Palm Trees in South Tunis." d'Aymeric. *Analyst*, 1921, 46, 243.

" The Rapid Production of Free Acids in Palm Oil." Balland. *J.S.C.I.*, 1918, 37, 774A.

" Notes on the Presence of a Gum in the Palm Fruit." E. Fickendey. *J.S.C.I.*, 1923, 42, 895A.

" The Commercial Manufacture of Palm Oil." V. Abeele. *J.S.C.I.*, 1924, 43, 564B.

" Free Fatty Acids in Palm Oil." A. C. Barnes. *J.S.C.I.*, 1925, 44, B45.

CHAPTER XXIII

COCONUT AND SIMILAR OILS

Coconut Oil

Coconut oil is obtained from the nuts of the coconut palm, *Cocos nucifera*, which is widely distributed in all tropical countries, especially along the coast-lines. Although the tree will grow in sub-tropical countries and also in somewhat exposed positions yet, under these conditions, the tree no longer bears fruit. It is thought that possibly the fact that the coconut palm grows so well near to the coast is due to the fact that common salt is more or less necessary to its growth, this idea being supported by the recent work at Porto Rico (*J. Jamaica Agri. Soc.*, 1923, 27, 673). The palm does not become fully fruit-bearing until it reaches an age of about ten years, but it first begins to flower at about six. The tree may continue to bear fruit for sixty years or even, in favourable circumstances, as long as one hundred years. Although the products of the trees have been used by the natives from prehistoric times, it is only within recent years that the cultivation of the palms has been seriously taken up, on what are supposed to be correct lines, with the result that as many as 6000 nuts per acre per annum have been obtained under good conditions. A good average annual crop for each tree is about 60 nuts, but these do not all ripen at the same time, which fact is particularly valuable as it enables the user to depend upon supplies practically all the year round.

The tree itself grows to a height of 60–100 ft. at maturity, and consists of a cylindrical stem from 18 to 24 inches in thickness, marked with rings where leaves have formerly grown, and terminating in a crown of from 16 to 20 graceful pinnate leaves each about 15 ft. long having a strong central rib on both sides of which are numerous long thin leaflets. The flowers grow enclosed in a spathe, each of which produces from five to fifteen nuts.

The nuts are enclosed in a thick fibrous outer husk, which is used for making mats, brushes and similar purposes. The inner hard dark-brown shell contains the white kernel which in turn contains a sweet milky fluid known as " coconut milk." For a description of coconut planting and the results obtained see Zaepernick (*J.S.C.I.*, 1911, 30, 1222), Pratt (*ibid.*, 1914, 33, 1096), and Cox, Brill, Parker and Yates (*J.S.C.I.*, 1918, 37, 96A and 97A).

Composition of Coconut Milk.—The liquid portion has been examined by several observers. Thus Behre (*Pharm. Zent.*, 1906, 20, 145) found that the specific gravity of three samples varied between 1·0244 and 1·0325, the extract between 5·8 and 7·7, the ash between 0·66 and 1·00, the proteins between 0·30 and 0·81, and that much of the solid matter was due to cane-sugar. The liquid has been recently examined by Matthews (*Analyst*, 1924, 49, 223). This observer found that the S.G. of three samples varied between 1·0421 and 1·0555, the solids between 9·9 and 13·0 and the $[\alpha]_D$ between 37·0 and 42·7. The liquid from one nut was examined more extensively. No starch was found. The ash was 1·25 W/V.; cane-sugar, 7·1; reducing sugar, 0·5. The liquid had a very feeble diastatic power and commenced to coagulate at temperatures above 43°.

Coconut Toddy.—Coconut toddy is a liquid which is collected in pots

from the unopened flower spathe by cutting off the end and allowing the liquid to trickle into collecting pots which are changed periodically. The methods of preparation and the composition of the resulting liquids, both before and after fermentation, have been studied by Gibbs (*J.S.C.I.*, 1911, 30, 1133) and by Browning and Symons (*J.S.C.I.*, 1916, 35, 1138), the latter paper in particular giving a very full and complete account of the industry as carried out in Ceylon. The toddy is used mainly for three purposes, namely, for the production of crude sugar (jaggery), as a beverage, and for the distillation of a potable spirit. For use as a source of sugar the liquid must, of course, be drawn unfermented. This is brought about by placing a small amount of slaked lime in the collecting pots each day—otherwise the liquid is in a state of active fermentation when it is collected. The following table shows the composition of fermented and unfermented toddy as given by Browning and Symons (*loc. cit.*).

TABLE CLVII.—COMPOSITION OF FERMENTED AND UNFERMENTED COCONUT TODDY

	Sp. gr. at 84° F.	Total Solids, grms. per 100 c.c.	Ash, grms. per 100 c.c.	Sucrose per cent.	Proteins per cent.	Alcohol per cent. by Weight.
1. Unfermented . .	1·058	15·19	0·33	13·5	0·32	..
2. Slightly fermented.	1·077	17·22	0·398	10·0	0·23	..
3. Unfermented . .	1·063	16·22	0·185	12·3	0·29	..
4. „ . .	1·060	15·82	0·31	13·75	0·26	..
5. „ . .	1·060	16·18	0·31	12·9	..	..
6. „ . .	1·061	16·28	0·31	12·6	..	..
7. „ . .	1·067	19·6	0·33	17·4	..	..
8. „ . .	1·065	17·0	0·39	..	..	..
9. „ . .	1·065	17·39	0·41	..	..	..
10. „ . .	1·067	19·68	0·11	17·4	..	..
11. Fermented . . .	1·001	2·43	0·38	..	..	5·8
12. „ . .	1·005	3·36	0·23	..	..	4·9

Coconut Fibre.—This is a valuable by-product in the coconut-palm industry. The method of production, at least as far as Ceylon is concerned, has been well described by Pratt as follows: " The best fibre is made by native methods, especially in the Galle district. The husks are placed in bamboo enclosures which are submerged in river or sea water. After about six days' softening they are beaten on a block, and the separated fibre hackled with a wooden comb and dried. Two classes of fibre are thus obtained, viz., " bristle fibre " (averaging 30 cm. in length) and " mattress fibre " which is spun into " coir yarn " about 17 m. long and 40 mm. thick. In the mills the fibre is softened in large tanks, iron rails being used to keep the husks submerged. After five days' soaking the material is crushed in a " breaker," and the fibres separated by revolving iron wheels (" drums ") studded with spikes. The long coarse fibres are hackled by hand, made into hanks and partially bleached with sulphur fumes. This is made into brushes, etc. The mattress fibre, consisting of torn and broken pieces falling from the spikes of the " drums," is spun into coir yarn and made

into mats and coarse cloths which are frequently dyed with aniline dyestuffs. Ceylon coir yarn is sold in the two grades of Kogalla and Colombo, which are further subdivided into 15 to 24 standards differing in thickness, colour, twist, etc."

Coconut Charcoal.—Coconut charcoal is prepared by burning the dried shells in pits with the usual exclusion of air. The product is now well known for its very high absorption properties, particularly of small quantities of rarefied gases and for this and other purposes it is in increasing use.

Copra.—Copra is the dried white " meat " of the coconut after it has been removed from the shell. The native method of producing this substance is to split the shells into two portions by hand labour, pour off the fluid and expose the two portions to the sun until dry, when the contraction of the meat allows it to become readily detachable from the shell. In some countries machines capable of dealing with 1000 nuts per hour have been installed. This method of sun-drying gives the finest product and also subsequently the best oil, but it is not possible in all climates and a quicker method of drying in kilns has been adopted in some cases—this method, however, gives a somewhat inferior product even under the best conditions. Smits has found (*J.S.C.I.*, 1918, 37, 33A) that 500 very ripe Java coconuts weighing 844 kilos yielded 127 kilos of copra (15 per cent.) whilst 500 nearly ripe nuts weighing 953 kilos yielded 129 kilos of copra (13·5 per cent.). He also found no material difference between nuts obtained from the coastal regions and those obtained inland.

Wells and Perkins (*J.S.C.I.*, 1922, 41, 987A) give an account of the use of sulphur fumes to prevent the growth of moulds to which copra, particularly some kinds, is very liable, the abstract states that: " The main cause of colour and rancidity of coconut oil is the action of moulds on the copra during drying. Where steam-drying is impracticable, sulphuring the copra is very satisfactory for the prevention of mould during air drying; 1 kg. of sulphur per charge of 3000 nuts is usually sufficient, and this is burnt in a pan on the floor of the sulphuring chamber, which may be about 4 ft. wide, 8 ft. long, 7 ft. high, the nuts being placed on trays piled one above the other on a trolley to facilitate removal. A preliminary sunning for an hour or so after opening the nuts is desirable, as the ' meat ' can then be separated more readily from the shells. The sulphured copra can be dried in two to three weeks in a shed without sunshine, if necessary, or more rapidly by sun-drying either on a floor or in light trays which can be stacked and covered up in case of rain. The direct protection against mould afforded by sulphur dioxide lasts about a month, but the copra is not susceptible to mould if once thoroughly dried and stored in a dry place."

The growth of moulds on copra is very highly destructive of the amount of oil present and Brill, Parker and Yates have shown that such loss may even exceed 40 per cent. (*J.S.C.I.*, 1918, 37, 97A).

Methods of Analysis of Copra.—The Association of German Oil Mills (*J.S.C.I.*, 1911, 30, 964) determines the amount of oil present by extraction in a Soxhlet apparatus at the temperature of the boiling-point of the solvent until no further oil is extracted—the material being removed from the thimble and re-ground once or twice during the extraction. Hoepfner and Burmeister (*J.S.C.I.*, 1912, 31, 396) use ether for the extraction, but this is not so suitable as petroleum ether as a considerable amount of non-fatty matter may be extracted by this solvent as indeed has been pointed out by Allen and Auerbach (*J.S.C.I.*, 1913, 32, 296). The composition of copra meal from which much of the oil had been expressed is given by Alvarez (*J.S.C.I.*, 1920, 39, 380A) as follows :

	Per cent.
Moisture	11·3
Oil	12·2
Crude proteins	20·1
Ash	5·5
Crude fibre	13·2
Carbohydrates	37·0
	99·3

The amount of oil in copra is usually about 65 per cent., although occasionally samples will contain as much as 75 per cent. The following table due to Schindler and Waschata (*Chem. Revue*, 1905, 27, 169) and quoted by Lewkowitsch (*Oils, Fats and Waxes*, Vol. II) gives a number of analyses of different varieties of kiln-dried and hot-air-dried copras.

TABLE CLVIII.—ANALYSES OF KILN-DRIED AND HOT-AIR-DRIED COPRAS (SCHINDLER AND WASCHATA)

No.	Origin.	Year.	Water.	Fat.
1	Ceylon	1900	..	71·40
2	„	1900	..	67·36
3	„	1901	3·65	69·17
4	Penang	1900	..	68·95
5	„	1900	..	67·08
6	Sangir	1900	..	68·93
7	Malabar	1900	..	71·03
8	Singapore	1900	..	69·05
9	„	1900	..	65·91
10	Java	1900	..	68·77
11	„	1900	..	67·06
12	„	1902	..	66·21
13	Pontianak	1900	..	65·43
14	Manila	1900	4·61	64·47
15	„ (special quality)	1900	..	67·55
16	„	1901	..	67·10
17	„	1901	..	68·57
18	„	1902	..	68·34
19	Pacific Islands	1900	4·10	74·72
20	Zanzibar	1901	..	70·23
21	Tangiers	1903	..	67·00
	Means of twenty-one analyses			68·30
	Maximum			74·72
	Minimum			64·47

Desiccated Coconut.—This product is prepared by breaking away the shells, washing the " meat " and shredding or granulating by machinery. The product is " desiccated " in special machines by means of a current

of hot air at about 90°, the moisture at the completion of the drying not being in excess of 2 per cent. The dried product is graded as to size by mechanical sieving and immediately packed for export.

Bolton and Revis (*Fatty Foods*, page 151) state that the presence of starch and sugar must be looked upon as adulterants, but Bodmer has shown (*Analyst*, 1920, 45, 18) that quite genuine dried coconut may contain as much as 7 per cent. of cane-sugar, the presence of which he ascribes to incomplete washing of the " meat " before desiccation.

Other useful papers bearing on coconuts and coconut cake are as follows :

" Comparative Keeping Qualities of Palm-kernel, Coconut, Ground Nut, and other Oil Cakes." Godden. *Analyst*, 1918, 43, 63.

" Nutritive Value of Coconut Globulin and Coconut Press Cake." Johns, Finks, and Paul. *J.S.C.I.*, 1919, 38, 384A.

" Extraction of Copra Cake with Solvents." West. *Analyst*, 1923, 48, 36.

" The Globulin of Coconut." Johns, Finks and Gersdorff. *J.S.C.I.*, 1920, 39, 169A.

The Production of Coconut Oil.—Coconut oil has been prepared by the natives of different parts of the world for centuries. The most crude of these methods was to cut up the dried kernel into small pieces and place in heaps in the sun when the oil which ran off was collected. Various modifications of this primitive method have been used, such as the previous pounding of the dried kernel and the exposure of the pulp so obtained to the heat of the sun in perforated vessels through which the liberated oil could run, a crude form of hand pressure being also employed in some cases. In those countries where the sun-heating process could not be relied upon a form of heating on rough trays formed from the coconut leaves over an improvised stove was also carried on. Better methods were carried out on the Malabar coast where the kernel pulp was treated with boiling water, the oil which rose to the top being skimmed off periodically. This gave a much better class oil, known then as Cochin oil, which quickly obtained a high reputation—a reputation which has held until the present time although " Cochin oil " now refers to a quality of oil (the highest) rather than the source from which it has been obtained.

By far the largest amount of oil is now obtained from imported copra, by expression, in Europe and America, in modern presses and is known as copra oil. A large quantity is, however, now being so pressed in the countries of origin and there is no doubt but that this amount will increase. For the production of coconut oil in this way the copra is ground in mills, moulded and pressed twice at a temperature of 55°–60°. Extraction with solvents has not yet reached any large proportions on account of the possible poorness of the resulting cake, but as this may be overcome easily by adding a proportion of unextracted cake, this method may yet be developed but in any case it is comparatively easy to control the amount of oil left in the cake as has been done at least at one works in this country for a number of years. The oil is refined by treatment with alkali which removes any free fatty acids and carries down colouring matters, proteins and other impurities. The native methods of production are described by Parker and Brill (*J.S.C.I.*, 1918, 37, 97A).

Coconut Cake.—Coconut cake, as has already been mentioned, is a valuable feeding-stuff particularly for dairy cattle, and large quantities are consumed for this purpose in this country. The following analyses will

give some idea as to the general composition of this article. The first six analyses are due to Smetham and Dodd (*J. Royal Lancs. Agri. Soc.*, 1921) and the two last to Wood and Halnan (*Composition and Nutritive Value of Feeding Stuffs*, Cambridge; University Press).

TABLE CLIX.—ANALYSES OF COCONUT CAKE

Name.	Water.	Protein.	Oil.	Carbo-hydrates.	Fibre.	Ash.
Coconut cake, English . .	9·01	21·19	9·20	43·04	11·91	5·65
„ „ „ (another make)	8·70	21·19	14·96	40·29	9·51	5·35
Coconut cake, Macassar .	9·30	18·75	16·96	40·56	8·98	5·45
„ „ Bombay . . .	11·90	23·12	11·83	35·70	7·90	9·55
Copra cake, Borneo . . .	10·70	19·75	10·28	44·16	9·61	5·50
„ „ Singapore . .	8·60	15·75	29·55	33·33	8·42	4·35
Coconut cake	11·4	20·7	9·9	41·4	11·2	5·4
„ „ meal . . .	11·3	19·5	6·7	42·5	13·6	6·4

TABLE CLX.—CONSTANTS OF COCONUT OIL

Authority.	$n^{40°}$.	S.G. 15·5° C.	Sap. Value.	Iodine Value.	R.M.	Pol.	Kirschner.	M.Pt. °C.	Sol. Pt.	Ti °C
Fryer and Weston .	35·5 ..	.. 0·926	.. 255–260	.. 8–9	.. 6·6–8	.. 15–18	.. ..	.. 23–26	.. ..	. 21
Bolton . .	1·4486–1·4492	.. ..	255–258 ..	7·9–8·8	6–8 ..	15–18 ..	1·6–1·9 ..	23–26 ..	22–23·5	. .
Trim *J.S.C.I.* .	1·4489 1·4491	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	24·85 ..	.. ..	. .

Properties.—Edible coconut oil is, in warm weather, a soft white fat, but somewhat brittle, breaking with a characteristic appearance, at temperatures below 15°. It has been commonly stated in the past and, in fact, is so stated even in current literature, that coconut oil easily becomes rancid, but this is not so in the case of samples which are properly prepared (cf. Walker, *Analyst*, 1906, 31, 165). The acrid, unpleasant state of the lower grades is due to decomposition both before and after expression due to unsatisfactory treatment (cf. Brill and Parker, *Analyst*, 1918, 43, 89; Perkins, *J.S.C.I.*, 1920, 39, 458A). "Thirty samples of edible coconut oil were kept for two years under varying conditions of light, air, etc. Oxygen was found to be necessary for the development of rancidity, but not of acidity. The action of light increased the hydrolysis of the fat in sealed bottles, but, on the other hand, all samples exposed to the air in darkness became rancid. Enzymes soluble in fat (but not those insoluble) appeared to have a slight effect, especially in increasing the acidity, but sterilisation of the oil had little, if any, beneficial effect. In the second stage of rancidity, the free fatty acids were oxidised to an extent depending upon the amount of

hydrolysis. This oxidation was accelerated by light and moisture, but light was not an essential factor. An oil with a low initial acidity remained sweet after exposure to air and light for two years." (Perkins, *loc. cit.*) Coconut oil is much more soluble in alcohol than are vegetable oils in general, in fact, with the exception of castor oil, coconut oil and oils of the same class are the most soluble of any. Milban has shown that coconut oil will dissolve completely in two volumes of absolute alcohol at 32° (cf. the Crismer test, page 92). The following results were obtained by van Kregten (*J.S.C.I.*, 1920, 39, 305A) for the critical temperature of solution of coconut and palm-kernel oils in alcohol and acetic acid respectively of various strengths:

TABLE CLXI.—SOLUBILITY OF COCONUT OIL

Solvent.	Sp. gr. at 15°/15° C.	Volume per cent.	Critical Temperature of Solution.	
			Coconut Oil.	Palm-kernel Oil.
Alcohol	0·7942	99·96	20·2	28·7
	0·7981	99·16	30·0	38·8
	0·8001	98·75	35·5	44·2
	0·8020	98·36	39·5	47·9
	Sp. gr. at 15°/4° C.	Per cent. Acetic Acid.		
Acetic acid	1·0573	99·25	17·9	32·5
	1·0579	99·05	26·0	41·5
	1·0584	98·85	30·9	45·6

Composition.—Coconut oil is characterised by containing large quantities of lauric and myristic acids which give to the oil its well-known properties; smaller quantities of acids of both lower and higher molecular weight are also present. Although a large number of other investigations had been carried out (such as those of Ulzer, Reijst, Kirschner, etc.) the whole of the fatty acids present in coconut oil were first definitely isolated by Haller and Youssoufian (*Analyst*, 1907, 32, 53) by the method of alcoholysis. These authors proved that, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic were present, that lauric and myristic acids predominate and that butyric acid could not be detected. These results have been confirmed by Elsdon (*Analyst*, 1913, 38, 8) who deduced the following quantitative composition for the mixed fatty acids:

Caproic acid	2
Caprylic acid	9
Capric acid	10
Lauric acid	45
Myristic acid	20
Palmitic acid	7
Stearic acid	5
Oleic acid	2
	100

but these figures, being liable to many sources of error are not very exact, they have, however, been confirmed in the main by W. N. Stokoe (*Analyst*, 1924, 49, 577). Cf. John Allan (*ibid.*, 1925, 50, 16). The caproic acid is probably a little higher, the capric lower and the lauric higher. Oleic acid also is probably a little higher. Walker has shown (*J.C.S.*, 1923, 123, 2837) that in a sample of coconut oil examined by him it was unlikely that more than 2 per cent. of capric acid was present and the author does not see at the moment any serious objection to this statement (cf. *Analyst*, 1924, 49, 275). It is an interesting fact that elm-kernel fat (Pavlenko, *Analyst*, 1912, 37, 201) is very similar in composition and is said to contain 56·2 per cent. of capric acid. A more recent analysis quoted by E. F. Armstrong, John Allan and Watson Moore, gives the following as the composition (*J.S.C.I.*, 1925, 44, 63T).

Caproic acid	..
Caprylic acid	9·5
Capric acid	4·5
Lauric acid	51·0
Myristic acid	18·5
Palmitic acid	7·5
Stearic acid	3·0 ?
Oleic acid	5·0
Linoleic acid	1·0

It would appear that even the qualitative composition of the oil is scarcely settled, at least, in regard to the presence of stearic acid, but there would seem to be little doubt but that it is present in at least some samples and it would be advisable to examine oils from various sources to decide finally whether stearic acid is actually absent from some oils.

The actual glycerides present in the oil have been examined by Bömer (*J.S.C.I.*, 1914, 33, 756) by distilling the oil in a high vacuum followed by fractional extraction and crystallisation of the distillates with acetone. He found the following esters: caprylolauromyristin, myristodilaurin, laurodimyristin, palmitodimyristin, stearodipalmitin, and also esters containing oleic acid which were not further examined. Caldwell and Hartley (*Analyst*, 1909, 34, 274) in an earlier paper obtained by the method of distillation in high vacuum about 60 per cent. of lauric acid and also isolated palmitic acid.

The odourous substances in coconut oil have been investigated by Haller and Lassieur (*Analyst*, 1910, 35, 356) who find, in addition to the free lower fatty acids, the presence of methyl-heptyl ketone, methyl-nonyl ketone, a trace of an optically active aldehyde, methyl-heptyl carbinol and methyl-nonyl carbinol.

Matthes and Ackermann (*Analyst*, 1908, 33, 357) found that coconut fat contains, in addition to the ordinary known phytosterol, a second phytosterol which forms a characteristic sparingly soluble tetrabromide, whilst Kedrovitsch (*Analyst*, 1912, 37, 497) found that the melting-point of the phytosteryl acetate (*vide* page 123) varied from 122° to 125°. Cf. Butter fat, page 400.

There is no specific test, with the exception of microscopic ones, that can be used for the detection of coconut oil (that of Ludwig and Haupt having been shown to be useless by Trimen, *Analyst*, 1913, 38, 246), although there are a number of qualitative methods which indicate oils of this class and other methods which, to a certain extent, differentiate between the

oils in the same class. The most widely used and, when carefully interpreted, the most useful of these is the one known as the Polenske method, which has been fully described on page 148. Many others have been suggested but none of these has any greater claims to consideration, although one or two are very useful for confirmatory purposes, particularly that of Shrewsbury and Knapp (the advantages of which are discussed on page 161) and some, e.g., those of Burnett and Revis (*Analyst*, 1913, 38, 255), Elsdon and Bagshawe (*Analyst*, 1917, 42, 72, 295, 298), and Stokoe (*J.S.C.I.*, 1921, 40, 57T), are necessary to decide the proportion of coconut oil present in any mixture where amounts of other oils of the same class may also be present.

The only qualitative test which is at all useful is a microscopic one and was devised by Hinks (1907, 32, 160). It is a useful confirmatory test when small quantities of coconut oil are suspected in admixture with other fats. The test is described by Hinks as follows: " Five c.c. of the melted and filtered fat are dissolved in twice the volume of ether in a tube, which is then packed in ice. After half an hour much solid glyceride has separated out, leaving a clear ethereal solution above. The ether is poured on to a plaited filter and rapidly filtered. The ethereal solution is evaporated on the water-bath, and the residual fat poured into a tube and boiled with three to four times its volume of alcohol (96 to 97 per cent. by volume). Complete solution takes place at the boiling-point. The solution is allowed to cool to room temperature, when most of the fat separates. The tube is then placed in water at 5°, and kept at that temperature for fifteen minutes. The alcoholic layer is rapidly filtered into another tube which is placed in a cooled chamber at 0°. A flocculent deposit soon separate; in this deposit are the crystals which indicate the presence of coconut oil: this is examined microscopically after being in the cold chamber for two or three hours. A portion is withdrawn by a wide-mouthed pipette placed on a slide and covered without pressure. To view the crystals satisfactorily a magnification of from 250 to 300 is required."

Hinks claims that the method will detect the presence of 5 per cent. of coconut oil in butter and most observers have confirmed this but the presence of certain other fats—notably lard—makes the indications of the test less trustworthy. Trimen (*Analyst*, 1913, 38, 246) claims that in the absence of coconut oil the method will distinguish between buffalo and cow butter fat and between sheep and goat butter fat respectively but as goat butter fat gives crystals resembling those of coconut oil care must be taken that a goat butter is not reported upon as a cow butter adulterated with coconut oil, particularly as goat butter fat frequently gives an abnormal Polenske value.

Several workers have attempted to make use of the solubility of coconut oil in alcohol as a means of the determination of the amount present in admixture with other oils. Ross (*Analyst*, 1908, 33, 457) went fully into this question and decided that with the methods that he adopted no useful results could be obtained. Arnold extracted the fat with alcohol, recovered the soluble portion and subjected this to the usual determinations. He obtained the figures contained in the following tables which are quoted by Lewkowitsch, but it is doubtful whether the method has many advantages, although these figures do show a tendency for the characteristic properties of coconut oil to become concentrated in the alcoholic extract.

TABLE CLXII.—ANALYSES OF FATS FOR ADMIXTURE OF COCONUT OIL

	Refracto-meter at 40 "Degrees."	Sap. Value.	R.M. Value.	Polenske.	Iodine Value.	Yielded Alcohol-Soluble Portion.
			American Lard			
Original lard . . .	50·1	194·9	0·33	0·55	62·5	..
Alcohol-soluble fat .	52·7	190·5	0·66	0·55	68·0	9·1g.
Alcohol-insoluble fat.	50·6	196·0	0·44	0·50	60·4	..
			German Lard			
Original lard . . .	47·7	193·8	0·55	0·50	49·0	..
Alcohol-soluble fat .	49·2	189·9	0·88	0·70	63·9	6·9g.
Alcohol-insoluble fat.	47·8	196·0	0·65	0·55	47·8	..
			German Lard			
Original lard . . .	48·4	195·7	0·44	0·60	53·2	..
Alcohol-soluble fat .	51·4	191·5	0·88	0·75	66·1	6·4
Alcohol-insoluble fat.	48·3	196·1	0·55	0·55	51·7	..
			American Lard Mixed with 2 per cent. of Coconut Oil			
Original fat . . .	49·8	195·4	0·55	0·60	62·0	.. ..
Alcohol-soluble fat .	51·0	194·3	2·50	1·25	64·4	12
Alcohol-insoluble fat.	49·8	196·0	0·55	0·55	60·4	..
			American Lard Mixed with 3 per cent. of Coconut Oil			
Original fat . . .	49·6	196·0	1·00	0·70	61·1	..
Alcohol-soluble fat .	49·3	205·5	4·13	2·35	60·5	9
Alcohol-insoluble fat.	50·0	197·7	0·90	0·75	59·9	..
			German Lard Mixed with 4 per cent. of Coconut Oil			
Original fat . . .	48·9	202·7	1·50	0·80	47·1	..
Alcohol-soluble fat .	49·1	216·2	5·70	3·50	45·7	9·9
Alcohol-insoluble fat.	49·0	201·6	1·10	0·70	46·3	..
			German Lard Mixed with 5 per cent. of Coconut Oil			
Original fat . . .	49·1	201·1	1·80	0·85	61·7	..
Alcohol-soluble fat .	48·7	210·0	5·56	3·24	55·3	9·1
			American Lard Mixed with 5 per cent. of Coconut Oil			
Original fat . . .	49·2	198·8	1·35	0·90	60·0	..
Alcohol-soluble fat .	49·0	210·6	5·60	3·95	52·7	9·1
Alcohol-insoluble fat.	50·0	197·1	1·00	0·75	58·8	..
			American Lard Mixed with 10 per cent. of Coconut Oil			
Original fat . . .	48·3	202·2	2·37	1·30	55·4	..
Alcohol-soluble fat .	46·9	229·0	8·00	7·85	39·7	10·2
Alcohol-insoluble fat.	49·2	200·0	1·90	1·10	55·5	..
			Butter Fat Containing 6 per cent. of Coconut Oil			
Original fat . . .	43·1	226·2	23·4	2·65	40·0	..
Alcohol-soluble fat .	40·6	235·2	34·6	3·8	41·2	35·59
Alcohol-insoluble fat.	44·05	221·8	20·3	2·2	39·5	..

The soaps obtained from coconut oil are sharply distinguished from those obtained from other oils in that they are not completely salted out even when the solution is saturated with salt. A method for the detection of coconut oil in cacao butter based on this fact has been suggested by Strube (*Analyst*, 1908, 33, 188) but experiments made by Bamford in the author's laboratory, with the idea of using this as a method for the determination of coconut oil, were not very successful as the results obtained were no more useful than those obtained by processes already well known. (Cf. Kerr, page 310.)

Examination of Coconut Oil.—On account of its comparative cheapness, coconut oil is quite infrequently adulterated although statements have been made to the effect that various seed oils have occasionally been used for this purpose. The Polenske value, saponification value and iodine values combined will, as a rule, quite readily show adulteration, although it must not be overlooked that the oil obtained from the outer rind of the coconut has a much higher iodine value than normal. Oil obtained from the rind has an iodine value as high as 40 and quite recently Armstrong and Allan have shown that this is a general feature not only of many varieties of coconut but also of other palms as well. They give the following tables (*J.S.C.I.*, 1924, 43, 212T; 1925, 44, 63T):

TABLE CLXIII.—COMPARISON OF OIL FROM THE WHOLE KERNEL AND KERNEL PARINGS OF THE COCONUT (ARMSTRONG AND ALLAN)

	Kernel Oil.		Parings Oil.	
	Saponif. Equivalent.	Iodine Value.	Saponif. Equivalent.	Iodine Value.
Malay States	214	7·2	244·2	28·9
Malabar (Cochin)	219	8·7	252·5	45·5
Java	214·5	8·5	253·1	59·7
Celebes Isles	216·5	9·6	249·7	25·0
Philippine Islands	216	7·3	241·8	33·1
Trinidad	216	8·0	246·0	37·2
Fiji Islands	217·5	8·5	237·0	32·1

TABLE CLXIV.—COMPARISON OF OIL FROM THE WHOLE KERNEL AND KERNEL PARINGS OF VARIOUS NUTS

	Kernel Oil.		Parings Oil.	
	Saponif. Equivalent.	Iodine Value.	Saponif. Equivalent.	Iodine Value.
Palm kernels	231·0	13·5	240·1	29·6
Babassu kernels	221·2	12·2	241·1	22·8
Brazil nuts	289·2	104·8	290·6	114·3
Almonds (sweet)	290·1	101·0	289·4	100·5
Arachis	296·0	97·0	296·0	95·0

It follows, therefore, that an oil prepared from copra consisting of an unusual proportion of the parings of the rind will have a higher iodine value than normal. Such oils, although possibly not adulterated, are certainly abnormal and should be treated as such. (Cf. F. Wittka, *J.S.C.I.*, 1925, 44, B998.)

The normal figures for coconut oil are saponification value, 255–260, iodine value, 7·8–9, Reichert value, 6·5–8, Polenske value, 15·5–18, and any oil having characters falling within these limits may be accepted as genuine provided that its physical appearance is normal and that there is no excessive amount of unsaponifiable matter. The percentage of unsaponifiable matter is usually about 0·2 per cent. but additions of solid hydrocarbons have been known in which case the amount of unsaponifiable matter may be considerably increased. The phytosterol of coconut melts after several crystallisations at 140·7 to 141·8, the acetate of which has a melting-point of about 128 to 130. Matthes and Ackermann (*Analyst*, 1908, 33, 357) have ascertained that coconut fat contains, in addition to the ordinary known phytosterol, a second phytosterol giving similar colour reactions, but combining by addition with two molecules of bromine, and yielding an acetate which forms a sparingly soluble tetrabromide which is characteristic. For instance, from 1 kilogram of cocoanut fat there were obtained 1·25 grms. of crude phytosterol, and 0·25 grm. of a liquid residue, as the result of a twice-repeated saponification, and shaking out with ether in a Hagemann's apparatus. The crude phytosterol melted at 135°–145°; after acetylation the product melted at 126°–128°. The acetylated product was then brominated in presence of ether and glacial acetic acid, and the characteristic tetrabromide then separated out in the form of thin plates, melting with decomposition at 180°–183°, and containing 39 per cent. of bromine. From the filtrate, after evaporation and recrystallisation from alcohol, crystalline aggregates of phytosterol acetate dibromide, melting-point, 132°–135°, were obtained.

Commercial samples of oil may contain large amounts of free fatty acids, quantities of 10 per cent. and over being sometimes found. The best qualities of edible oil should not, however, contain more than 0·1 per cent. of free acid calculated as lauric acid, whilst the upper limits for moisture and unsaponifiable matter are 0·25 and 1·0 per cent. respectively. (Committee of Analysts to Ministry of Food, 1919.)

Determination of Coconut Oil in Mixtures.—The difficulty of determining the exact amount of coconut oil when present in admixture with other oils was early recognised (it is due to the fact that the analytical figures are not proportional to the amount of coconut oil present) and already in 1911 Cribb and Richards (*Analyst*, 1911, 36, 327), recognising that this variation in the Reichert and Polenske values was due to the solubility of the " insoluble " acids in the Reichert acids, proposed that a fixed amount of 1·9 should be added to the Polenske value and subtracted from the Reichert value, whilst Arnaud and Hawley (*Analyst*, 1912, 37, 122) modified this where the values were low. The matter was later reinvestigated by Elsdon and Smith (*Analyst*, 1925, 50, 53), who found that this correction factor of 1·9 was only accurate for one set of figures and that it varied both with the amount of coconut oil and also with the amount of butter fat if present. These corrections can be taken from the table below and it will be noticed that that for the Reichert, although of the same order as that for the Polenske, is not identical with it. The table is used by finding the appropriate correction figure for the experimental value and adding it (taking into account the algebraic sign) to the latter.

TABLE CLXV.—CORRECTIONS FOR OBSERVED REICHERT AND POLENSKE VALUES (COCONUT OIL)

Polenske Values.				Reichert Values.			
Observed Value.	Correction to be added. Percentage of Butter.			Per cent. CNO from Polenske.	Correction to be subtracted. Percentage of Butter.		
	0.	5.	10.		0.	5.	10.
1·0	0·4	−0·1	−0·2	0	0·0	0·1	0·2
1·5	0·7	0·0	−0·2	5	0·3	0·3	0·3
2·0	0·9	0·5	−0·2	10	0·6	0·5	0·3
2·5	1·5	0·6	0·2	15	0·9	0·9	0·6
3·5	2·0	1·5	0·9	20	1·2	1·0	0·9
5·0	2·4	1·8	1·5	30	1·5	1·4	1·4
7·0	2·2	2·0	1·7	40	1·3	1·1	0·8
8·0	1·7	1·6	1·3	50	1·1	1·0	0·5
9·0	1·2	1·2	0·9	60	0·6	0·4	0·0
10·5	0·5	0·7	0·5	70	0·7	0·5	0·3
12·0	0·0	0·0	−0·3	80	0·7	0·5	0·3
14·0	−0·2	−0·6	−0·6	90	0·4	0·2	0·0
16·0	−0·1	−0·3	−0·7	100	0·0	..	..

When the corrected Polenske figure has thus been obtained the percentage of coconut oil may be calculated from the equation,

$$\% \text{ C.N.O.} = \frac{(P - 0{\cdot}2 - 0{\cdot}03B) \times 100}{17{\cdot}6}.$$

Where P is the corrected Polenske value and B the percentage of butter fat.

In cases where butter is also present the amount may be calculated from the corrected Reichert value (corrected in a similar manner) using the formula

$$\% \text{ butter fat} = \frac{R - 0{\cdot}065 \times C - 0{\cdot}2}{0{\cdot}284}.$$

Where R is the corrected Reichert value and C the percentage of coconut oil calculated from the Polenske value.

The author considers that the above formulæ give the most accurate results that can be obtained by what is, after all, not an absolute process, but the work of Bolton, Richmond and Revis (*Analyst*, 1912, 37, 183) gives results which are fairly accurate and their formulæ have the advantage of simplicity; they are quoted on page 412. Cassal and Gerrans (*Analyst*, 1910, 35, 519) modified the Polenske method by steam-distilling the fatty acids from a calcium chloride solution bath at about 145°. In this way the insoluble acid figure for coconut oil was increased from 17, as it is in the Polenske method, to about 66 but as, at the same time the figure for butter was increased to 15, in place of the 2·5–3·0 given by the Polenske method, the ratio of the figures for butter and coconut oil is not improved upon and it is this ratio which, after all, is the important point.

The Distinction of Different Oils of the Same Family.—The formulæ given above are only applicable when coconut oil is not accompanied by palm kernel or some other similar oil or by stearine prepared from them. The only oil that at the moment is likely to be used is palm-kernel oil, but other oils such as babassu-kernel oil are likely, at any moment, to be imported in quantity so that the possibility of their presence must not be overlooked. The only oil, apart from coconut oil, that has been worked out in any detail up to the present is palm-kernel oil and tables for its determination when present in mixtures are given on page 341.

For the detection and determination of palm-kernel oil and coconut oil when present together in mixtures, a problem which is not easy on account of the great similarity between them, several methods have been suggested. The first was that of Burnett and Revis (*Analyst*, 1913, 38, 255) which depends upon the alcohol solubility of the barium salts of the Polenske acids. The method is carried out as follows:

The ordinary Reichert-Meissl-Polenske determination is made in the STANDARD apparatus and by the STANDARD method. The Polenske figure is obtained using N/10 baryta. The insoluble barium salts are then filtered off on a hardened filter-paper under pressure, and the salts washed three times with 3 c.c. of 93 per cent. alcohol (by vol.), the funnel being kept covered during filtration and washing. The paper, after all possible alcohol has been sucked out, is dropped into a wide-mouthed CO_2 flask, ten times the Polenske value in c.c.'s of 93 per cent. alcohol (by vol.) added, and the flask boiled under a reflux condenser till the barium salts are in solution. About 5 c.c. of the hot solution are then poured rapidly into a strong test-tube (6 inches × ½ inch), which is at once closed with a stopper carrying a small bulb thermometer and an aluminium wire stirrer. The liquid is rapidly stirred, holding the tube in a good light, and the turbidity point noticed. The liquid is then warmed till again clear, and the turbidity point again noted. This second temperature is taken as the turbidity temperature. If desired, the tube can be fixed in a wide tube, so as to obtain slower cooling.

Working in this manner, coconut oil gives a turbidity temperature of 52·5° and palm-kernel oil, 68·5° and mixtures of these fats give temperatures between these limits proportionate to the percentage composition. The turbidity point is very sharp, is independent of the outside temperature, and the barium salts, on which the test depends, are quite insoluble in the cold alcohol used for the Polenske determination. The turbidity points are also quite independent of the amounts of the two fats present in the original sample, but determine their relative percentages, and so supply the necessary information. The strength of alcohol (93 per cent. by volume) must be strictly adhered to if the values here given are to be employed. It is the most satisfactory concentration. Other oils and fats (such as are likely to be present) do not interfere. In certain cases small quantities of barium salts are insoluble in the boiling alcohol. In such cases a clear solution cannot be obtained. The turbid liquid is therefore poured into a long test-tube, corked, and kept upright in a water-bath at 70° to 71° until the solid matter has settled. The clear supernatant liquid is then poured off into the turbidity tube and the temperature of turbidity determined. This process does not affect the results. This PERMANENT turbidity, due to barium salts of acids other than those derived from coconut and palm-kernel oils, must be distinguished carefully from that due to palm-kernel "stearine." The barium salts of the insoluble volatile acids of this "stearine" do not dissolve in ten times the Polenske value in cubic centimetres of 93 per cent. alcohol,

but the liquid becomes more turbid immediately the flask is removed from the water-bath.

The following table gives results which have been obtained by these authors:

TABLE CLXVI.—TURBIDITY TEMPERATURES

Fat.	Reichert-Meissl.	Polenske.	Turbidity Temperature. °C.
Coconut oil	7·5	16·5	52·5
Palm-kernel oil	5·2	9·6	68·5
„ " oleine "	7·2	12·1	59·5
„ " stearine "	...	8·2	72·5
Coconut " oleine "	..	..	53·0 } Calc.
„ " stearine "	..	..	63·0 } Calc.
„ " oleine," 80 per cent. Palm-kernel " oleine," 20 per cent.	8·24	17·05	54·5
Coconut " stearine," 60 per cent. Palm-kernel " stearine," 40 per cent.	4·43	9·93	67·0

Another method has been devised by Stokoe (*J.S.C.I.*, 1921, 40, 57T) which depends upon the melting-point of the Polenske acids; this process is carried out in the following way: In the standard Reichert-Polenske process, after distilling 110 c.c. the liquid is cooled and the insoluble acids collected on a filter; the condenser tube is rinsed down with 20 c.c. of warm water (30°–40°), which is poured over the filter. The filter-paper is washed with warm water (30°–40°), and as soon as the last drop of water has drained through, several capillary tubes (internal diameter of 1 mm.) are filled to the depth of $\frac{1}{2}$ in. with the now melted acids. Two of the tubes are immediately attached, one on either side, by means of a small rubber band, to a thermometer graduated to read 1/10°, and the thermometer fitted into a test-tube by means of a cork having a hole through which the thermometer is placed. The tube is supported in a beaker containing ether, the surface of which should be above the level of the acids in the capillary tubes. A rough idea as to whether the bulk of the acids is from palm kernel or coconut will have been obtained from the appearance of the acids in the original Reichert-Polenske distillate. If the acids are solid at ordinary temperature it is necessary to warm the ether to about 30°. A gentle stream of air is forced through the ether by means of a foot bellows so as to lower its temperature gradually, the rate of cooling being so adjusted that the temperature of the ether is 2° below that registered by the capillary tube thermometer. As the cooling progresses the fatty acids will become slightly cloudy, then a distinct " seeding " or crystallising will occur. At the first appearance of crystals the temperature is noted. This " seeding-point " is quite definite and sharp. At this point the acids in the capillary tubes appear liquid with a number of tiny white crystals along the sides of the tube. It is important in performing the test that the rate of cooling should be regular.

The following tables show the results obtained by Stokoe by this method:

TABLE CLXVII.—STOKOE'S RESULTS ON MIXTURES CONTAINING ONLY COCONUT AND PALM-KERNEL OILS

Coconut.	Palm-kernel.	"Seeding" Point. °C.	Average. °C.
Per cent.	Per cent.		
85	15	11·8 11·6 11·6 .. / 11·9 11·6 12·0 12·0	11·8
75	25	13·5 13·4 13·2 13·2 / 13·2 13·5 13·2 13·0	13·4
60	40	15·7 15·3 15·6 15·6 / 15·4 15·3 15·3 15·6	15·5
50	50	16·9 17·0 / 16·8 17·0	16·9
40	60	17·9 17·9 / 17·9 18·0	17·9
25	75	19·6 19·4 / 19·4 19·5	19·5
10	90	21·6 22·0 / 21·7 22·0	21·8

Four samples of coconut oil of different origin and the same number of palm-kernel oil were examined. The highest figure for the "seeding-point" of coconut oil acids was 11·4° and the lowest, 9·9°; average, 10·75°. The figures for palm-kernel acids were: highest, 23·2°; lowest, 22·05°; average, 22·75°.

TABLE CLXVIII.—STOKOE'S RESULTS ON MIXED FATS

1.—CONTAINING 30 PER CENT. OLEO, 10 PER CENT. COTTON-SEED OIL, 60 PER CENT. COCONUT OR PALM-KERNEL OIL OR MIXTURES OF THEM

Relative Proportions of Coconut and Palm-kernel Oils.	"Seeding" Point. °C.	Average. °C.
Coconut 100 per cent.	11·3 11·6 11·3 / 11·3 11·5 11·4	11·4
Palm-kernel 100 per cent. . . .	23·5 23·7 / 23·5 23·7	23·6
Coconut 75 per cent., palm-kernel 25 per cent.	14·5 14·0 / 14·5 14·1	14·3
Coconut 50 per cent., palm-kernel 50 per cent.	17·6 17·6 / 17·5 17·5	17·55
Coconut 25 per cent., palm-kernel 75 per cent.	20·4 20·9 20·6 / 20·4 21·0 20·3	20·6

2.—Containing 50 per cent. Oleo, 20 per cent. Cotton-Seed Oil, 30 per cent. Coconut or Palm-Kernel or Mixtures of Them

Relative Proportions of Coconut and Palm-kernel Oils.	"Seeding" Point. °C.				Mean. °C.
Coconut 100 per cent.	12·0	12·0	12·0		12·0
	11·9	12·0	12·0		
Palm-kernel 100 per cent. . . .	24·0	24·0	..		24·0
	24·0	24·1	..		
Coconut 33 per cent., palm-kernel 66 per cent.	20·0	19·6	19·9	19·8	19·8
	20·1	19·5	19·8	19·7	
Coconut 50 per cent., palm-kernel 50 per cent.	17·8	17·2	17·8	17·7	17·7
	18·2	17·3	17·6	17·8	
Coconut 66 per cent., palm-kernel 33 per cent.	16·6	16·2	16·2		16·3
	16·4	16·2	16·4		

It will be observed that the presence of other fats raises the "seeding-point," but that, roughly speaking, parallel lines are given on the graph. Thus in the analysis of an unknown fat mixture it will be necessary first to ascertain the approximate quantity of the coconut group of fats present by determining the saponification value and the Reichert-Polenske value. Reference is then made to the corresponding line or intermediate line if necessary on a graph diagram,* and from this the relative proportions of coconut and palm-kernel oils are read off.

Stokoe states that the method can be readily carried out as an extension of the standard Reichert-Polenske method, the contents of the capillary tubes being added to the alcoholic solution of the remainder of the insoluble acids and the whole being titrated as usual to obtain the Polenske value.

The following table shows the results obtained by Stokoe on margarine samples of known composition.

Table CLXIX.—Stokoe's Results on Margarine of Known Composition

Relative Proportion of Coconut and Palm-kernel in Sample.	Sap. Value.	Reichert Meissl.	Polenske.	"Seeding" Point. °C.	Relative Proportion of Coconut and Palm-kernel indicated.
Palm-kernel 100% .	228·7	4·05	6·1	23·5	100% P.K.
,, 100% .	208·2	1·36	1·3	24·0	100% P.K.
Coconut 100% . .	223·7	5·01	6·4	11·8	100% C.N.
,, 100% . .	246·3	7·15	13·0	11·5	100% C.N.
,, 50% . } Palm-kernel 50% }	244·1	5·61	11·2	16·9	51% C.N. 49% P.K.
Coconut 25% } Palm-kernel 75% }	228·1	4·35	7·3	20·6	26% C.N. 74% P.K.

* A graph is given in the reference cited above.

The method has recently been examined at some length by Gilmour (*Analyst*, 1925, 50, 119). As a result of this work Gilmour arrived at the following conclusions :

1. In mixtures containing only coconut and palm-kernel fats the determination of the melting-point of the insoluble volatile acids enables the quantity of either fat to be estimated to within 5 per cent. of the actual amount present.

2. In mixtures containing coconut or palm-kernel fat or both, and at the same time other fats, (1) holds when the per cent. of coconut group fats is above 70. When the per cent. is below 70, the method is not sufficiently accurate to enable the coconut and palm-kernel fats to be separately determined, but they can be estimated together as the percentage of coconut group fats with an accuracy of approximately 5 per cent. When mixtures come under this category the melting-point will often indicate whether coconut or palm-kernel fat or both fats are present, and also which of the two predominates.

In the original paper, which should be consulted, a large number of tables are given. The following are selected for reproduction here :

TABLE CLXX.—MIXTURES OF COCONUT AND PALM-KERNEL FATS

Coconut Fat per cent.	Palm-kernel Fat per cent.	Total Distillation Figure.	M.Pt. of Insoluble Volatile Acids. °C.
100	0	21·0	9·6
90	10	20·2	9·7
80	20	19·5	11·1
70	30	18·7	12·5
60	40	18·0	14·2
50	50	17·2	15·0
40	60	16·5	16·6
30	70	15·7	17·5
20	80	15·0	20·0
10	90	14·2	20·9

TABLE CLXXI.—MIXTURES OF COCONUT FAT AND LARD

Coconut Fat per cent.	Lard per cent.	Total Distillation Figure.	M.Pt. of Insoluble Volatile Acids. °C.
100	0	21·0	10·0
80	20	16·9	10·3
60	40	12·8	12·0
40	60	8·8	14·8
20	80	4·7	19·0
10	90	2·6	26·1
0	100	0·6	45·1

It is to be regretted that these determinations were not carried out with the more generally used Polenske process.

A third method and, possibly, in some respects a better method, has been suggested by Elsdon (*Analyst*, 1917, 42, 298) which depends upon the relationship between the amount of coconut oil indicated by the Polenske value and that indicated by the Shrewsbury and Knapp value (page 158). The reason for this is that coconut and palm-kernel oils give practically identical Shrewsbury and Knapp values, whilst, of course, the Polenske values are considerably different. It follows, therefore, that palm-kernel oil is indicated in those cases where the amount of coconut oil calculated from the Shrewsbury and Knapp value is greater than the amount calculated from the Polenske value.

In cases where palm-kernel (the possibility of the presence of some other oil of like character must not be lost sight of) oil has been indicated by any of the above processes a check may be obtained by means of a study of the relationship between the Reichert and Polenske values of the mixture. In the absence of butter fat (in the presence of butter fat the amount can

TABLE CLXXII.—REICHERT AND POLENSKE VALUES OF COCONUT AND PALM-KERNEL OILS

Palm-kernel Oil per cent.	Process.	Percentage of Coconut Oil.										
		0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
0	Reichert	0·6	2·0	3·3	4·4	5·2	5·7	6·3	6·6	6·9	7·2	7·4
	Polenske	0·4	1·4	2·3	3·5	5·1	6·8	9·4	11·8	13·8	15·2	16·8
10	Reichert	1·2	2·5	3·6	4·7	5·5	6·1	6·5	6·8	7·0	7·3	..
	Polenske	1·2	2·1	3·6	4·8	6·5	8·4	10·6	12·4	14·6	16·6	..
20	Reichert	1·8	3·3	4·2	5·0	5·7	6·3	6·6	6·9	7·2	..	..
	Polenske	1·7	2·6	4·4	5·4	7·6	9·6	11·5	13·3	15·4	..	..
30	Reichert	2·2	3·7	4·7	5·2	5·9	6·5	6·7	7·0	..	..	..
	Polenske	2·5	3·6	5·1	7·2	8·8	10·3	12·5	14·4	..	..	..
40	Reichert	2·6	4·0	5·0	5·5	6·2	6·6	6·8	..	..	..	..
	Polenske	3·2	5·1	6·8	8·4	9·5	11·8	14·0	..	..	..	..
50	Reichert	3·1	4·4	5·3	5·8	6·4	6·7	..	..	..	..	..
	Polenske	4·3	6·0	8·0	9·3	11·2	13·0	..	..	..	..	..
60	Reichert	3·5	5·0	5·6	6·1	6·6	..	..	..	..	..	..
	Polenske	5·6	7·6	9·1	10·8	12·6	..	..	..	..	..	..
70	Reichert	3·9	5·2	5·9	6·3	..	..	..	..	..	..	..
	Polenske	6·2	8·5	9·7	12·3	..	..	..	..	..	..	..
80	Reichert	4·3	5·5	6·1	..	..	..	..	..	..	..	..
	Polenske	7·4	9·5	11·5	..	..	..	..	..	..	..	..
90	Reichert	4·7	5·6	..	..	..	..	..	..	..	..	..
	Polenske	8·6	10·6	..	..	..	..	..	..	..	..	..
100	Reichert	4·8	..	..	..	..	..	..	..	..	..	..
	Polenske	9·7	..	..	..	..	..	..	..	..	..	..

be determined by the Kirschner process and allowed for) the Reichert and Polenske values will have, should coconut oil only be present, the definite relationship shown in the table on page 341, but where a greater or less amount of palm-kernel oil is present this relationship is altered, as shown above, the Reichert being proportionately less or greater. From a consideration of this table, along with the others mentioned, a very close approximation to the actual amounts of the oils present can be made.

Where the determination of the amounts of these oils present in a mixture is at all important a mixture should be made having a composition similar to that which has been assigned to the unknown substance and the experimental results obtained with the two mixtures, determined under similar conditions and in the same apparatus, compared.

Other methods have been suggested for the determination of coconut oil and the calculation of the amount present in mixtures from the results obtained. Thus Gilmour (*Analyst*, 1921, 46, 183) makes use of the M.Pt. of the Polenske acids and his method may be used with advantage as a confirmatory test. Other and less important suggestions have been made by Meurice (*J.S.C.I.*, 1921, 40, 484A) and by van der Laan (*J.S.C.I.*, 1923, 42, 287A). An oxidation method proposed by Hodgson has, unfortunately, proved to be unreliable. (*Analyst*, 1908, 33, 49, 122, 189.)

Coconut Oleine and Stearine.—Coconut oil is at times separated into the lower and higher melting constituents. The natives, for example, frequently express a portion of the oil in the cold and obtain an oil which is used locally as an edible oil and which does not come on the market in any quantity. Such an oil has a M.Pt. of about 20°. A certain amount of coconut stearine is produced for use as a cacao butter substitute and for such a produce Lewkowitsch has suggested the name " chocolate fat " a name which, in the opinion of the author, is, for obvious reasons, highly objectionable. The oleine is usually used for soap making.

The following constants have been obtained for these products by various observers:

TABLE CLXXIII.—CONSTANTS OF COCONUT STEARINE AND COCONUT OLEINE

1.—COCONUT STEARINE

Observer.	Sap. Value.	Iodine Value.	R.M. Value.	Polenske Value.	M.Pt.	Titre Test.
Sachs	252	4·0–4·5	3·4	..	29·5	27·4
Knapp	..	..	3·9–4·2	11·1–12·1	..	..
Blichfeldt	252–258	3·8–9·4	..	..	26·4–32·0	..
Lewkowitsch	251–257	4·0–6·6	3·3–6·3	..	..	26·4

(*Analyst*, 1908, 33, 123. *Ibid.*, 1912, 37, 3. *J.S.C.I.*, 1919, 38, 150T.)

2.—COCONUT OLEINE

Observer.	Sap. Val.	Iodine Value.	R.M. Value.	Polenske Value.	M.Pt.	Titre Test.
Knapp	..	..	8·5	23·2	..	..
Lewkowitsch	265	14·8	8·0	..	..	20·3

" The Determination of Alkali and Soap in Coconut Oil." W. L. Brooke. *J.S.C.I.*, 1924, 43, B986.

" The Determination of the Fatty Acids in Coconut Oil Soaps." J. Grossfeld. *J.S.C.I.*, 1925, 44, B214.

Palm-Kernel Oil

Source.—The oil is obtained by expression or extraction from the kernels of the palm fruit *Elæis guineensis*. The fruits, which are described under palm oil on page 315, usually contain one kernel, although palms cultivated in East Africa somewhat frequently contain two. As far as England is concerned the trade in palm kernels (the kernels are usually imported as such and much oil is expressed in Hull and Liverpool) has entirely arisen since the European War of 1914–1918 and almost the whole of the imports which now amount to over 200,000 tons per annum are used for home consumption. The kernels are exported from West Africa more than half coming from Nigeria.

After the pulp of the fruit has been removed for the preparation of palm oil the nuts are dried and then cracked. Until quite recently the cracking of the nuts was done by striking each one separately between two stones, obviously a slow and laborious operation and one which does not lead to a high output. Several attempts have been made to introduce portable nut-cracking machines which are now being used to a considerable extent to supplement manual labour in spite of the cheapness of the latter. It is quite possible that methods will be improved and the oil palm cultivated on sound lines thereby improving the quality and output of the products.

The kernels are screened, separated magnetically and ground between rollers. The expression is usually carried out in two stages, the second at about 60°, the first at some 10° lower. The kernels contain about 49 per cent of oil, the usual variations being from 44–53.

Palm-kernel cake is a valuable feeding stuff for cattle which has come into some prominence during comparatively recent years. From experiments which have been carried out by various observers (*Analyst*, 1918, 43, 63; 1919, 44, 204; 1921, 46, 138; *J.S.C.I.*, 1915, 34, 1108; 1916, 35, 860, 1231), the cake is very readily digestible, improves the yield of milk and compares favourably with other cakes in its keeping properties.

Composition.—The composition of palm-kernel oil was first elucidated by Valenta who found caproic, caprylic, capric, lauric, myristic, palmitic and oleic acids. Jensen found butyric acid to be absent. The subject has been further investigated by Elsdon (*Analyst*, 1914, 39, 78) and by E. F. Armstrong and Allan (*J.S.C.I.*, 1924, 43, T207) who find the approximate relative amounts of the fatty acids present as follows.

	Elsdon.	Armstrong and Allan.
Caproic . . .	2	..
Caprylic . . .	5	3
Capric . . .	6	6
Lauric . . .	55	50
Myristic . . .	12	16
Palmitic . . .	9	6·5
Stearic . . .	7	1·0
Oleic	4	16·5
Linolic . . .	..	1·0

E. F. Armstrong, John Allan and Watson Moore (*J.S.C.I.*, 1925, 44,

143T) have reinvestigated the problem and find the following composition together with traces of caproic acid:

Caprylic acid	3%
Capric acid	3%
Lauric acid	52%
Myristic acid	15%
Palmitic acid	7·5%
Stearic acid (?)	2·5%
Oleic acid	16%
Linoleic acid	1%

Salway (*J.S.C.I.*, 1917, 36, 1184) has discovered about 0·1 per cent. of methyl-nonyl ketone in the oil to which at least a portion of the odour of the oil is ascribed.

The actual glycerides present have been examined by Bömer (*J.S.C.I.*, 1923, 42, 1232A) and by Bömer and Schneider (*J.S.C.I.*, 1924, 43, B478). These authors were unable to detect the presence of caproic or stearic acids and they found that palm-kernel oil was composed almost entirely of the following glycerides. Caprylo-myristo-olein, M.Pt., 13·9°; myristo-dilaurin M.Pt., 33·4°; lauro-dimyristin M.Pt., 40·0°; palmito-dimyristin M.Pt., 45·2° and myristo-dipalmitin M.Pt., 51·4°. It is not easy to reconcile the work of these various observers. Both Bömer and Schneider and Armstrong and Allan failed to find caproic acid, although the fraction obtained by Elsdon by the method of alcoholysis boiling at 63°–76° at 14 mm. could scarcely be anything else but methyl-caproate. It would seem desirable that further work should be done on this question to discover how oils from varying sources may differ in composition. Heiduschka and Burger (*J.S.C.I.*, 1915, 34, 668) found caproic acid but no stearic.

TABLE CLXXIV.—CONSTANTS OF PALM-KERNEL OIL

Authority.	Sap. Val.	Reichert.	Polenske.	I.V.	n^{40}.
[1] Heiduschka and Burger	253·4	6·6	9·4	15·0	..
[2] Ellis and Hall	..	..	..	16–23	..
[3] Trim	..	..	..	..	1·4510
[4] Fryer	..	..	10·5	..	..

[1] *J.S.C.I.*, 1915, 34, 668. [2] *J.S.C.I.*, 1919, 38, 128T.
[3] *J.S.C.I.*, 1920, 39, 307T. [4] *J.S.C.I.*, 1918, 37, 262T.

Palm-Kernel Stearine.—Sachs (*Analyst*, 1908, 33, 124). M.Pt., 32°; Reichert, 2·2; Sap. val., 242; I.V., 8; titre, 28·5°.

The following constants have been found by André and Guichard for what they call "Murumuru, an American palm-kernel fat."

M.Pt.	34–35 C.
$d^{15/15}$	0·918
n_D^{31}	1·4535
Saponification val.	240–241·5
Iodine value	11·2–11·5
Reichert	2·8–3·1
Polenske	6·9

Caprylic and capric acids were found but no caproic and also possibly arachidic.

Properties and Special Tests.—Palm-kernel oil is practically indistinguishable in appearance and properties from coconut oil to which it is so closely allied in composition. The chief difference between these oils is the considerably lower amount of volatile acids which is contained in palm-kernel oil as is shown by the considerably lower values obtained for the Reichert and Polenske values.

As is the case with coconut oil, palm-kernel oil is not very likely to be adulterated, but tests for purity may be applied along the same lines as those

TABLE CLXXV.—REICHERT, POLENSKE AND KIRSCHNER VALUES OF PALM-KERNEL OIL

Palm-kernel Oil per cent.	Process.	Percentage of Butter Fat.								
		0.			2.			10.		
		Expt.	Calc.	Diff.	Expt.	Calc.	Diff.	Expt.	Calc.	Diff.
0	Reichert	0·6	See Coconut Oil Table							
	Polenske	0·4								
	Kirschner	0·2								
20	Reichert	1·8	1·4	−0·4	2·3	2·0	−0·3	4·6	4·3	−0·3
	Polenske	1·7	2·3	0·6	1·7	2·3	0·6	1·9	2·5	0·6
	Kirschner	0·5	0·4	−0·1	0·9	0·8	−0·1	2·9	2·6	−0·3
40	Reichert	2·6	2·3	−0·3	3·2	2·9	−0·3	5·2	5·2	0·0
	Polenske	3·2	4·1	0·9	3·2	4·1	−0·9	3·5	4·3	0·8
	Kirschner	0·6	0·5	−0·1	1·0	0·9	−0·1	3·0	2·7	−0·3
50	Reichert	3·1	2·7	−0·4	3·6	3·3	−0·3	5·6	5·6	0·0
	Polenske	4·3	5·1	0·8	4·3	5·1	0·8	4·7	5·3	0·6
	Kirschner	0·8	0·6	−0·2	1·1	1·0	−0·1	3·2	2·8	−0·4
60	Reichert	3·5	3·1	−0·4	4·0	3·7	−0·3	6·0	6·0	0·0
	Polenske	5·6	6·0	0·4	5·6	6·0	0·4	6·0	6·2	0·2
	Kirschner	0·9	0·7	−0·2	1·3	1·1	−0·2	3·3	2·9	−0·4
70	Reichert	3·9	3·5	−0·4	4·4	4·1	−0·3	6·5	6·4	−0·1
	Polenske	6·2	6·9	0·7	6·2	6·9	0·7	6·6	7·1	0·5
	Kirschner	0·9	0·8	−0·1	1·3	1·2	−0·1	3·5	3·0	−0·5
80	Reichert	4·3	4·0	−0·3	4·7	4·6	−0·1	6·9	6·9	0·0
	Polenske	7·4	7·8	0·4	7·5	7·8	0·3	7·8	8·0	0·2
	Kirschner	0·9	0·8	−0·1	1·3	1·2	−0·1	3·5	3·0	−0·5
90	Reichert	4·7	4·4	−0·3	5·1	5·0	−0·1	7·3	7·3	0·0
	Polenske	8·6	8·8	0·2	8·6	8·8	0·2	8·9	9·0	0·1
	Kirschner	0·9	0·9	0·0	1·3	1·3	0·0	3·6	3·1	−0·5
100	Reichert	4·8	..	..	..	..	..	..	..	..
	Polenske	9·7	..	..	..	..	..	..	..	..
	Kirschner	1·0	..	..	..	..	..	..	..	..

Butter = Reichert 28·5, Polenske 2·2, Kirschner 22·0

for coconut oil on page 334. The normal figures for palm-kernel oil are saponification value, 247, iodine value, 15–20, Reichert value, 5·5, Polenske value, 10, and any oil having characters of this nature may be accepted as genuine, provided that it is apparently normal in other respects. The general standards for purity of edible palm-kernel oils are similar to those for coconut oil, page 324, in fact most of the remarks on coconut oil apply with almost equal force to palm-kernel oil.

There are no special tests for palm-kernel oils beyond the determination of the Reichert, Polenske, Kirschner values and deduction from these and from the various methods of distinguishing palm-kernel from coconut oils as outlined on pages 334 *et seq.* The proportion of palm-kernel oil present in a mixture from which coconut oil is absent may be determined from the formula

$$\%\text{P.K.O.} = \frac{(P - 0{\cdot}2 - 0{\cdot}03B) \times 100}{10}.$$

Where P is the corrected Polenske obtained by adding the appropriate correction from the above table to the experimental value and B is the percentage amount of butter fat if present.

When coconut oil is present in addition to palm-kernel oil, the methods for ascertaining this are fully given on pages 334, etc., the table on page 341 must be used and in addition it may be advisable to use the Shrewsbury and Knapp method which gives practically identical results with palm-kernal and with coconut oils. (Cf. The kernel oil of *Cocos syagous* and other kernel oils under palm oil, page 320.)

Atta-Seed Oil

This oil is obtained from the seeds of *Pentaclethra macrophylla*, the seeds of which are known by various names by the natives of West Africa, such as Maboula Panza, Attawa, Atta, Odu, Fai, Owala, Fulla Panza, Nulla Panza, Opochala. The seed oil of *Pentaclethra Filamentosa* is somewhat similar and is known as Paroa-caxy. The oil has not come into general use, as up to the present no quantity of the oil has reached this country. Bolton and Hewer, however, consider that the oils from both sources may be edible so that supplies may arrive at any time.

Table CLXXVI.—Characteristics of Atta-Seed Oil

Authority.	S.G. 15°.	M.Pt. °C.	Sap. Value.	Iod. Value.	n^{40}.	Titre. °C.	R.M.	Pol.	Free Acid %	Unsa %
Lewkowitsch . .	0·916	22–24	168–203	86–99	1·4654	52	..	..	..	..
Wagner and Muesmann (*J.S.C.I.*, 1914, 33, 1098)[3].	0·916	..	181·9	99·5	1·4637	..	6·5	0·5	10·3	..
[1] Bolton & [2] Hewer (*A.*, 1917, 42, 43)	0·917	18·4	181·3	100·4	1·4644	..	..	..	0·08	1·3
	..	..	177·0	69·0	1·4612	..	..	..	0·20	..

[1] = *P. macrophylla.* [2] = *P. Filamentosa.*

[3] (Cf. *ibid.*, 1906, 25, 893; 1907, 26, 699; 1910, 29, 1019.)

Bolton and Hewer state that the oil of *P. macrophylla* is mixed with that of *Irvingia barteri* to make " Dika bread."

Babassu-Kernel Oil

Source.—This oil is obtained from the kernels which are derived from a species of Attalea probably *A. funifera*, Mart, which is closely allied to the Cohune palm (*A. Cohune*, Mart). This grows to a considerable extent in Brazil where it is known by a variety of names as Caco babassu, Bassoba, Curcia, Coquilho, Coquilla, Cognito and Vaua-assu. The fruits have been carefully described by Bray and Elliott (*Analyst*, 1916, 41, 298) and by Bolton and Hewer (*ibid.*, 1917, 42, 42), the latter authors giving a useful illustration. The kernels contain from 65–68 per cent. of oil which may be extracted in a similar manner to palm-kernel oil. Bray and Elliott stated in 1916 that " At first the oil was extracted by hand-shelling but machinery has now been installed and supplies on a large scale may be expected." Several thousand tons have actually been received in this country but oil pressers and manufacturers are not prepared to accept comparatively small quantities when future deliveries cannot be guaranteed. For this and other reasons the oil has not come into general use. The kernels contain about 4·5 per cent. of moisture and 65 per cent. of fat.

The press cake should prove to be a valuable feeding stuff as it has a nutritional value about equal to coconut cake and somewhat superior to palm-kernel cake.

Composition.—The composition of this oil has not yet been fully elucidated but it resembles coconut oil and palm-kernel oil, being closely allied to the latter. It is very similar to Cohune kernel oil although it has a somewhat higher iodine value.

Table CLXXVII.—Characteristics of Babassu-Kernel Oil

Authority.	S.G. 100°/15°.	Sap. Value.	Acid Value.	Iodine Value.	R.M.	Polenske.	M.Pt. °C.	Unsap. Matter.
Bray and Elliott . .	0·868	249	5·5	15·6	5·8	10·2	26	..
Bolton and Hewer . .	..	246·9	2·8	16·3	..	..	26·1	0·3
Gardner . .	..	261	..	14	..	..	..	..

The oil itself being cheap is not likely to be adulterated but it is quite possible that if and when it becomes a commercial proposition, it will be used as a substitute for cacao butter and similar purposes. The methods of detection and determination are similar to that for palm-kernel oil (q.v.). As in the case of other oils of this family it is possible that the ratio of the Reichert to the Polenske value will be of assistance in the determination of the amount present in mixtures but no work along these lines has yet been done on this oil.

References.—Bray and Elliott, *Analyst*, 1916, 41, 298. Bolton and Hewer, *ibid.*, 1917, 42, 42. Gardner, *J.S.C.I.*, 1923, 42, 728A. Cf. *J.S.C.I.*, 1915, 34, 1061.

Cohune-Nut Oil

This oil is obtained from the kernels of the cohune palm, *Attalea cohune*, Mart., a plant which is abundant in British Honduras and neighbouring countries. Although the tree is so abundant and the supplies of the fruit almost unlimited these products have not been exploited to any great extent. This is due to some extent to the difficulty in cracking the nuts which are extremely hard. Machines for this purpose have been introduced into British Honduras but do not seem to have been particularly successful. On the other hand large amounts of palm-kernels are even now obtained by hand labour so that the possibility of the appearance of quantities of this oil on the market are not remote.

The fruits resemble the babassu fruit and contain one or more kernels which, however, are shorter and rounder than babassu kernels. The kernels contain 65–70 per cent. of a white crystalline fat resembling coconut oil in appearance and smell. Very little work has been done on the values of this oil so that the figures given in the following table must not be taken as being the extreme limits for this oil. It is desirable that further figures be obtained for this oil, and also for oils of the same class. (*Analyst*, 1913, 38, 433; 1914, 39, 396; 1916, 41, 300; 1921, 46, 100.)

Table CLXXVIII.—Values of Cohune-Nut Oil

Observer.	S.G. 100°/15°.	Acid Value.	Sap. Value.	Iodine Value.	R.M.	Pol.	Unsap. per cent.	Titre. °C.	M.Pt. °C.	n^{40}
Imperial Institute	0·864 0·871	1·2– 20·4	252·4– 256·5	11·0– 13·7	6·8 & 8·3	12·5 to 15·4	0·23 0·28	19·7– 21·0	.. ..	.. ..
Clayton .	..	..	254– 260	9– 12·5	..	..	..	25– 29	22– 24	1·44 1·44

Various other species of *Attalea* have been examined from time to time. Thus Grimme (*Analyst*, 1910, 35, 536) examined the oil from a species of *Attalea* (possibly *A. spectabilis*) found in America from the mouth of Rio de la Plata to Honduras. He found the constants given in the table below. The oil from *A. spectabilis* has been examined at the Imperial Institute (*Analyst*, 1921, 46, 50). It was described as curua palm-kernel oil and is considered by Bolton to be identical with babassu oil; the constants are given below. The Imperial Institute also described another species of *Attalea* closely related to the Corozo palm previously described (*Bull. Imp. Inst.*, 1917, 15, 479) as *Scheelea* or *Attalea excelsa* but now thought to be more nearly applied to *Scheelea insignis*. The fat resembles coconut oil in its general properties. Figures are given in the following table :

TABLE CLXXIX.—COMPARISONS OF OILS FROM VARIOUS SPECIES OF ATTALEA

Observer.	M.Pt.	n^{40}.	Acid Value.	Sap. Value.	Iodine Value.	R.M.	Pol.	Unsap. per cent.	Titre. °C.	M.Pt. Acids. °C.
rimme . .	24·5	1·4491	8·1	256·6	3·6	..	..	1·08	..	38·5
mperial Institute . .	23·6	1·4470	1·2	259·5	8·9	6·3	15·6	0·36	24·6	..
mperial Institute . .	24·0	1·4490	2·3	250·9	10·8	8·6	10·8	0·4	..	..

[1] *A. spectabilis*, curua palm oil. [2] *Scheelea insignis*, " Mamarron."

Some older figures for some of the species of *Attalea* (*A. maripa*) are quoted by Lewkowitsch under the heading of maripa fat, where the tree is stated to be indigenous to the West Indies and the kernels to be known in Brazil as Urukuri nuts. The commercial fat is stated to be obtained from several species including *Maximiliana maripa*, Drude (cf. *M. regia*, Mart, below).

TABLE CLXXX.—VALUES FOR MARIPA FAT

Observer.	M.Pt. °C.	Sap. Value.	Iodine Value.	R.M.	Titre. °C.	M.Pt. Acids. °C.
Maeceuw . . .	26·5	270·5	17·4	4·5	25	27·5–28·5
Bassière	23	259·5	9·5	..	..	..
Frank & Gnädinger	18·5	349	16·0	10·5	..	..

The results of Frank and Gnädinger are interesting as their saponification value is very high and supports their statement that the fatty acids of the oil consist largely of caproic, caprylic and capric acids. They state that the oil was obtained from *A. excelsa*. The results should be compared with those which the Imperial Institute obtained for the species of *Attalea* allied to *Scheelea insignis* showing that there would appear to be a considerable difference in the composition of these oils.

Cokerite-Kernel Oil.—This oil, which is obtained from *Maximiliana regia*, Mart., resembles cohune-nut oil and the other oils of the same class. The nuts and the oil have been described by Bray and Elliott (*Analyst*, 1916, 41, 299) and by Bolton and Hewer (*Analyst*, 1917, 42, 39). The fruits resemble to some extent cohune nuts and are more pointed and somewhat smaller. The structure of the fruits is analogous to those of the oil-palm. The pericarp is tough and fibrous externally but soft and pulpy internally. This pericarp contains about 15 per cent. of oil resembling palm oil having acid value, 28·6; saponification value, 211·6; iodine value, 51·4 and titre,

25·5. The kernels yield about 60 per cent. of a hard cream-coloured fat similar to palm-kernel oil. Figures for the oil are given below.

TABLE CLXXXI.—VALUES FOR COKERITE-KERNEL OIL

Observers.	M.Pt. °C.	Titre. °C.	Acid Value.	Sap. Value.	Iodine Value.	R.M.	Pol.	Unsap. per cent.	n^{40}.
Bray and Elliott .	27	24·2	3·1	253	13	3·0	7·0	0·3	..
Bolton and Hewer .	28·5	..	0·7	240·9	16·6	..	..	..	1·4513

DIKA FAT

Dika fat is prepared from the seeds of various species of *Irvingia* such as *I. barteri* and *I. gabonensis* which grow largely along the coast of West Africa. The kernels are used together with the seeds of *Pentaclethra macrophylla* in the preparation of Dika bread which is a staple article of food among the natives (Bolton and Hewer, *Analyst*, 1917, 42, 35). The substance is prepared by removing the kernels from the shells, grinding them with a small quantity of water and seasoning material and finally moulding into cakes.

The nuts (and sun-dried nuts) were first examined by Lewkowitsch (*Analyst*, 1905, 29, 394) who found that the kernels contained 54 to 66 per cent. of fat. He could not detect stearic acid by the Hehner and Mitchell method, which does not, of course, prove its absence, and the acids may be taken as consisting for the most part of lauric and myristic. The fat has been and may be used for edible purposes, particularly as a cacao butter substitute. The following characteristics have been observed:

TABLE CLXXXII.—VALUES OF DIKA FAT

Observer.	M.Pt °C.	Acid Value.	Sap. Value.	I.V.	R.M.	Pol.	n^{40}.	Titre. °C.	Unsap. per cent.
Lewkowitsch . .	38·9	1·8–12·6	244–250	3·3–5·2	0·4	..	..	34·8	0·73
[1] Grimme. . . .	41·3	4·0	241·2	4·3	..	..	1·4542	38·1	1·43
[2] Imperial Institute .	39·2	..	244–250	3·3–4·2	..	..	..	..	..
[3] Sprinkmeyer and Diedrichs . . .	33·0	4·0	242·0	2·9	0·2	5·5	1·4498	..	..
[4] Sachs	..	..	..	5·2	..	..	..	..	..

[1] *Analyst*, 1910, 35, 536. [2] *Analyst*, 1909, 34, 164.
[3] *Analyst*, 1912, 37, 349. [4] *Analyst*, 1908, 33, 123.

Other species of *Irvingia* (e.g. *I. oliveri* which is indigenous to Cochin-China) yield the so-called cáy-cáy fat. This has been examined by Bontoux who found that the seeds yielded 22 per cent. of kernels containing 60 per cent. of a white hard and brittle fat having the following characteristics as quoted by Lewkowitsch:

TABLE CLXXXIII.—VALUES OF CÁY-CÁY FAT

	Fat extracted in the Laboratory.	Native Preparations.	
		No. 1.	No. 2.
Fat—			
Melting-point, °C.	39·7	38·2	38·4
Solidifying-point, °C.	31	31·2	31·8
Saponification value	235·0–235·6	236·3	237·4
Iodine value	6·7–6·8	4·1–4·2	4·9–5·1
Acid value	0·89	23·5	34·9
Fatty acids—			
Fatty acids + unsaponifiable, %	94·0	93·4	93·2
Solidifying-point (titre test °C.)	36·6	..	36·4
Neutralisation value	253·0	..	250·2
Mean molecular weight	222	..	224

PARAGUAY PALM-NUT OIL

Paraguay palm oil is obtained from the kernels of *Acrocomia sclerocarpa*, a tree similar to the coconut palm, which is widely distributed in South America and which forms large forests in Paraguay. Lewkowitsch describes the oil as mocaya oil or as Macaja butter. There is some confusion between this oil and gru-gru oil which is also stated to be obtained from *A. sclerocarpa*, but the Paraguay kernels (which are smaller than but otherwise indistinguishable from gru-gru kernels) contain a somewhat higher percentage of fat of decidedly softer consistency and higher iodine value. Bray and Elliott (*Analyst*, 1916, 41, 299) state that: "In view of our limited knowledge of South American palms and the difficulty of identifying the species from the seeds or fruits alone, it is quite probable that 'gru-gru' and 'Paraguay' kernels are not identical in origin." This conclusion is supported to some extent by Bolton and Hewer who find (*Analyst*, 1917, 42, 38) higher iodine values and lower saponification values for the Paraguay palm oil. The palm is thus described by these writers:

"The tree grows to a height of 20 to 30 feet in Bahia, and forms large forests in Paraguay. The fruits are of a somewhat similar structure to tucum fruits, but the outer pulp is enclosed in a thick, smooth shell. The proportion of the parts is as follows:

Outer shell (epicarp)		28
Mesocarp:	Oily pulp	24
	Inner shell (endocarp)	42
Kernel		6
		100

Pulp Oil.—This oil is analogous to commercial palm oil, has a somewhat similar smell and consistency, and is of a golden-yellow colour. The oil is suitable for soap manufacture, and if obtained from fresh fruits, so that there is not more than 10 per cent. of free acids, it could be refined for margarine-making. Its value is slightly below that of palm oil.

These authors determined the following characteristics for the pulp oil:

Solidifying-point, °C.	24·9
Saponification value	189·8
n_D^{40}	1·4527
Iodine value	77·2
Acid value	110

The Paraguay kernels (which contain about 65 per cent. of oil) and kernel oil are described by Bray and Elliott (*loc. cit.*) in the following way: " The ' Paraguay ' kernels are roughly spherical, about 12 mm. in diameter, and weigh about 1 grm. each; the skin is almost black and the flesh much softer than that of ordinary oil-palm kernels (*Elæis* sp.). The fat is decidedly softer than either coconut or palm-kernel oil, being only semi-solid at ordinary temperature, and the iodine value is higher than that of either of these oils, or than that of the oils derived from the other kinds of palm-kernels examined. The residual cake of ' Paraguay ' kernels is even richer in protein than coconut cake, and should have, therefore, a high feeding value. The kernels are stated to have sold recently in Liverpool at prices between those of fine palm kernels and copra."

The following characteristics have been obtained by the observers above quoted:

Table CLXXXIV.—Characteristics of Paraguay Palm Nut Oil (Bray and Elliott, Bolton and Hewer)

	Bray and Elliott.	Bolton and Hewer.
Melting-point, °C.	..	22–25·8
Titre, °C.	21	..
Acid value	26·1	0·8–9·0
Saponification value	247	237–246
Iodine value	28·5	16–30
Unsaponifiable matter	0·3	..
Reichert	6·5	..
Polenske	10·2	..

Kernels and oil described as " gru-gru," and stated to be obtained from *A. sclerocarpa*, have been mentioned by various workers. A. W. Knapp (*J.S.C.I.*, 1914, 33, 9) states that " gru-gru " is the Trinidad name for *A. sclerocarpa*. He describes the tree and its fruits at some length and states that one tree he examined had nine large bunches, each one containing 400 fruits, or 3600 in all. The Imperial Institute have also reported upon this palm (*J.S.C.I.*, 1914, 33, 147) in the following way: " The gru-gru palm is a native of the West Indies and South America and is widely distributed in Trinidad but does not usually occur in such abundance as to enable kernels to be exported commercially, while there is a local demand for kernels for edible use. This palm also occurs in Grenada, St Vincent, St Lucia and the Leeward Islands. The nuts had a hard, brittle, woody shell about $\frac{1}{8}$ inch in thickness; the kernels resembled oil palm kernels (*Elæis guineensis*).

Trials showed that the nuts could be shelled fairly well by a palm nut-cracking machine. The kernels contained about 7 per cent. of moisture and 56–57 per cent. of fat resembling coconut and palm-kernel oils."

The oil has also been examined by Bray and Elliott (*Analyst*, 1916, 41, 298) the results being given in the following table along with those of Knapp.

	Bray and Elliott.	Knapp.
Melting-point, °C.	..	26·0
Titre, °C.	20·5	23
Acid value	1·4	1·2
Saponification value	254–255	243·5
Reichert value	5·7–6·8	7·2
Polenske value	10·0–12·6	13·9
Iodine value	16·2–21·0	19·4
Unsaponifiable matter %	0·4–0·5	..
Specific gravity 100°/15°	0·868	0·861

The coyal palm would seem to be closely allied to those mentioned above, and the following description from an American official report (*J.S.C.I.*, 1915, 34, 1061) should be compared with those given for the above oils: "This tree grows very abundantly in Costa Rica, Nicaragua, and upper Panama, especially on the Pacific side. It is stated that the nuts can be gathered in great quantities and very cheaply. At present cattle eat them where they fall. Specimens of the nuts examined by the Bureau of Plant Industry of the Department of Agriculture, have been identified as *Acrocomia vinifera*, Oerst., and contained 57·7 per cent. of petroleum ether extract. An analysis of the seed oil of the same palm from Nicaragua was published in 1903 as follows: sp. gr. at 25° C., 0·9136; M.Pt., 25° C.; clouding-point, 17° C.; free acid, 1·69 per cent.; saponification value, 246·2; iodine value, 25·2; Reichert-Meissl value, 5. Both the oil and residue are similar in composition to that obtained from the coconut and other palms, and could be used in the manufacture of similar food products. The difficulty of producing this oil in commercial quantities, however, is a mechanical one, there being no machinery on the market at present that can be economically used for cracking the extremely hard shells that inclose the kernels."

According to Fendler the seeds are slightly roasted by the natives, ground to a paste, slightly warmed by exposing to the sun, and expressed in sacks between warmed iron plates.

The fat of a closely allied plant, *A. totai*, Mart., has been examined by Grimme, but the results obtained are more or less different from those of the other oils (*J.S.C.I.*, 1910, 29, 1019):

Unsaponifiable matter	13·4 per cent.
Saponification value	188
Iodine value	26·9
n_D^{40}	1·4525
Titre, °C.	28–30

Tucan-Kernel Oil

Tucan kernel oil is obtained from the kernels of the palm *Astrocaryum vulgare*, which is described on page 300. The kernels, which contain some 45 per cent. of fat, weigh about 3·5 grms. each. The fat is similar to palm-kernel oil but is harder and has a somewhat higher melting-point. It should be of value for all those purposes for which palm-kernel oil is used. The following characteristics have been observed:

TABLE CLXXXV.—VALUES OF TUCAN-KERNEL OIL

Observer.	Sol. Pt. °C.	M.Pt. °C.	Sap. Value.	I.V.	R.M.	Pol.	n_D^{40}.	Titre.	Unsap. per cent.
Bontoux . .	26	29–30	243	10·4–11·2	..	..	..	..	..
[1] Bray and Elliott . .	..	30·5	249	11·6	3·8	5·9	..	27	0·3
[2] Bolton and Hewer .	28·6 ..	30·6–32·5	240–245·2	.. 12·2–13·9	.. ..	.. ..	1·4497 1·4505	.. ..	.. ..

[1] *Analyst*, 1916, 41, 299. [2] *Analyst*, 1917, 42, 35.

A somewhat similar oil has been obtained from the kernel of the Murumuru palm by Bolton and Hewer. This oil is stated to be similar to coconut stearine and should, therefore, be of the greatest value commercially. The fruit weighs about 12 grms. of which nearly half is kernel—practically no oil is contained in the pericarp; the kernels contain about 40 per cent. of oil which, in the hands of the above workers, gave the following characteristics :

Melting-point °C.	34
Solidifying-point °C.	32·5
Saponification value	237·0
n_D^{40}	1·4501
Iodine value	12·4

Another fat from another member of the *Astrocaryum* species has also been examined by the Imperial Institute (*Analyst*, 1922, 47, 124). This fat, which is also closely allied to *A. tucuma*, Mart., is obtained from the kernel, which contains some 37 per cent. of fat. The nuts consisted of 60 per cent. shell and 40 per cent. kernel. The fat, which was pale cream in colour and fairly hard, had the following characteristics :

Specific gravity 100°/15°	0·864
Melting-point °C.	35·5
Titre °C.	29·7
Acid value	1·7
Saponification value	249·6
Iodine value	9·4

CHAPTER XXIV

ANIMAL FATS

Beef Fat

Beef Tallow

Source.—Beef fat is obtained from all parts of the bodies of oxen, cows and calves. The milk fat, of course, is not included in this as it is the chief constituent of butter (q.v.). The external fat is largely used in the manufacture of soap and candles and for these purposes, especially in the smaller establishments, the fat from the different parts of the body is frequently not separated. For edible purposes, however, the internal fat, particularly the kidney fat, is alone used and where edible grades are manufactured the internal fat is kept separate and subjected to different processes. This fat from the kidneys before separation from the connective tissues is known as suet (and even after separating it is frequently sold as shredded suet after cutting into small shavings with the help of rice flour) and after separating by the process described below the finest qualities are known as *première jus*. It is this *première jus* before or after separation of the stearine which is used as a normal constituent of edible fats but the better grades of tallow from the body fat are sometimes used as an adulterant of lard.

The old method of rendering fats was to employ the direct heat of open fires, which resulted in inferior products and also in the trade of fat-melting being scheduled as a noxious trade. The next method to be employed was that of heating by steam coils in open pans and although this was a great improvement some of the older objections still held good although to a lesser degree. For these reasons closed vessels known as digesters are now used almost exclusively. These are usually closed vertical boilers of iron or steel (sometimes lined with tin or lead) with a perforated false bottom. The material to be treated is chopped up and placed on the false bottom. The man-hole which is provided is then closed and steam at varying pressures is admitted. The liberated fat floats on the surface of the condensed steam and is withdrawn through appropriate cocks. The residual tissue still retains a considerable amount of fat. In order to liberate this it is usual to treat the residue with very dilute sulphuric acid, which coagulates to a certain extent the cell tissues so that on a further treatment with steam the oil is liberated. The second operation yields a somewhat inferior fat to the first but the proportion of sulphuric acid used is not sufficiently high to produce hydrolysis, so that the proportion of free fatty acids in the fat is not increased.

The tissues intended for the preparation of *première jus*, i.e., those surrounding the kidneys, are rendered in much the same way but in this case the temperature is not allowed to rise above 45°. The tissues are first hardened by immersion in iced water, then shredded in special machines, treated with salt to assist the separation and rendered in a suitable digester. In this case, of course, the acid rendering is not used, or should not be used, for oils intended for edible purposes. The rendered fat is refined from the last traces of tissue, etc., by remelting, adding salt and allowing to settle. The refined fat is then allowed to cool, usually in shallow tin-lined trays,

until the stearine has separated out in a crystalline condition. The solid fat is cut up into blocks, wrapped in canvas press-cloths and subjected to mechanical pressure in hydraulic presses. In this way the " stearine " (known as " oleostearine " or " beef stearine ") is removed and the oil which flows from the presses is known as oleo oil; the more solid material is stearine. These two substances are used in varying amounts for the production of edible fats, the proportion being varied according to the melting-point desired for the product and to the amount and properties of the other ingredients present.

Composition.—The fatty acids consist principally of stearic, palmitic, and oleic acid. The amount of stearic and palmitic acids varies from 33–50 per cent., that of oleic from 50–60. There seems to be very little doubt but that small quantities of other unsaturated acids are present—thus Farnsteiner found small quantities of linolic and linolenic acid. It has been suggested by some observers that this is due to the influence of feeding with oil-cakes. It has been suggested that lard differs from beef (or mutton) fat in that it contains notable amounts of myristic acid which is absent from beef fat. This statement is by no means borne out by the results of Myddleton and Barry, who find in beef fat 2·5 per cent. of myristic, 27 per cent. of palmitic, 25 per cent. of stearic, 43 per cent. of oleic and 2·5 per cent. of linolic, whereas in lard (q.v.) they find no myristic acid at all. The actual glycerides which are present is still a matter to be settled, but the presence of mixed glycerides seems to have been proved. Kreis and Hafner (*Analyst*, 1904, 29, 259) stated that they found palmito-distearin by crystallisation of beef fat. Bömer (*Analyst*, 1907, 32, 357) had no difficulty in obtaining tristearin and isolated about 1·5 per cent. from beef fat and 4·5 per cent. from a sample of commercial pressed-beef tallow. Dekker (*J.S.C.I.*, 1922, 41, 333A) by means of fractional freezing out obtained three groups of crystals with melting-points of 70°, 63° and 58° respectively. The presence of tristearin, distearopalmitin and dipalmitostearin was deduced and the tristearin was afterwards isolated by repeated recrystallisation from ether.

The composition of the fat varies both with the food of the animal and with the part from which the fat is taken. The internal fat is the hardest

TABLE CLXXXVI.—ANALYTICAL FIGURES FOR BEEF FAT

Authority.	S.G. 15°/15°.	M.Pt. °C.	Sap. Val.	I.V.	$n_D^{40°}$.	Titre of Fatty Acids. °C.	R.M.	Acid Valu
Lewkowitsch . .	860– 100°/ 862 0°	43– 48·5	193– 200	35·6 47·5	1·4584– 1·4586	43– 45	0·25	..
Fryer and Weston	937	47–	193–	42	1·4573–	43–	0·5	Edible
	953	49	198	45	1·4584	45		not over
Evan's Reports . .	940	..	192–	35–	1·4574	..	..	..
	950	..	200	45	1·4584	..	..	1–50
Mitchell . . .	952	43–	194–	38–	..	..	0·25	..
	..	48	198	44	..	..	..	..
Leach	943	40–	192–	35–	1·4586	38–	0·5	3·5–50
	952	45	200	47	..	46	..	..
Bolton	..	..	193–	38–	1·4573	43–	..	Edible
	..	..	199	44	1·4857	45	..	below 1·

with M.Pt. of about 50°—that from the back and legs may fall to very little over 40°. This difference in M.Pts. is due, of course, to the difference in the relative proportion of the solid and liquid glycerides present.

Beef fat (tallow) is, as a general rule, not used as such for edible purposes except as an adulterant for lard and similar products. The first grades known as *première jus* and its products, oleo oil and oleo or beef stearine are used in the manufacture of margarine and other food products. The analytical figures for oleo oil and beef stearine, which are frequently separated before use as edible fats, will depend upon the pressure and temperature used in their preparation. The iodine value may be reduced to only a few units with a corresponding increase in the melting-point but, as a general rule, the following figures may be taken as the average values of those products with which one is likely to meet.

	M.Pt. °C.	$n_D^{40°}$.	I.V.	Sap. Value.	Titre. °C.
Oleo oil	30–35	1·4580	40–50	197–200	..
Oleostearine	50–55	1·4570	15–25	193–197	48–51

Properties and Special Tests.—The edible qualities are pale-yellow to white in colour, free from disagreeable odour and almost tasteless. The various special tests for beef fat depend upon the particular glycerides which occur and not to any extent upon the actual fatty acids present. The problem of detecting an admixture of beef fat in other fats is by no means easy, and although it would certainly be possible to detect 10 per cent. of beef stearine under certain conditions, yet in other cases such an admixture might pass entirely undetected and, moreover, as is pointed out under lard (page 364), certain samples of hog fat show characteristics which are distinctly suspicious.

The first work on the subject was carried out by Husson in 1878 and on this the well-known test of Belfield was based (*Analyst*, 1888, 13, 70). In the original Belfield method 40 drops of melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool. The test tube is closed with cotton-wool and allowed to stand in a cool place until crystallisation has taken place. The crystals so obtained are examined microscopically; beef fat gives a deposit of curved tufts of thin needles radiating from a point. This method has been studied by Stock and others for the detection of beef fat in lard. Full details of the methods suggested are given under lard, page 364. Other valuable methods for the detection and determination of beef fat are those of Polenske (the difference value, page 366) and Bomer (page 366) which are described elsewhere.

Examination for Adulteration.—Beef fat is not frequently adulterated, but in those cases where it is, its detection is not difficult. The Reichert and Polenske values should not be more than about 0·5, the iodine value should not be much over 45. In the case of oleo oil and oleo stearine the figures will vary, of course, according to the melting-point and must be interpreted in conjunction therewith, the lower the melting-point the higher the permissible iodine value. Lard is the only substance which would cause difficulty, but fortunately this is not a very likely adulterant, for this reason very little work has been done on this subject, and in the present state of knowledge it would not be possible to detect small (possibly accidental)

additions. Larger proportions would influence several of the characteristics and would materially change the microscopical appearance of the crystals obtained by crystallisation from ether as described on page 366. A test for beef fat in cacao butter (*A.O.A.C.*) is described on page 307.

Suet.—The internal fat of oxen and sheep is used for various purposes as suet. It is scarcely possible to distinguish these two fats by chemical means, but there are certain differences in their microscopic appearance, texture and odour which may be used where necessary to differentiate them. Comparison should be made with known genuine samples of various kinds. Until comparatively recent times suet was sold in its natural state so that adulteration was unlikely if not impossible, but now a large amount of what is known as " shredded suet " is on the market from which, in general, all the tissue has been removed and which, therefore, is susceptible of adulteration. It has been stated that cotton-seed oil is sometimes used for this purpose, but no case has yet come under the writer's notice.

For the preparation of shredded suet the finest edible beef fat should be used—*première jus* or oleo stearine being a very usual material. The solid fat is forced through small circular holes by means of hydraulic pressure. The threads so formed are then covered with rice flour (or ground rice) and transferred to the chopping machine where they are cut up into small lengths suitable for use—the rice flour acting as a buffer, preventing the pieces from sticking together. These small pieces are then placed in a sieving machine where excess of the rice flour is removed and where any larger particles which have escaped the chopping machine are also removed to be returned for further treatment. The fat is then ready for packing.

Although, as has been remarked above, the possible presence of foreign oils must not be overlooked, the more likely method of adulteration is the presence of an excess of rice flour—either deliberately added or accidentally left in. The more reputable firms use every effort to keep the percentage of flour down to about 10 per cent. but 15 per cent. may be taken as a reasonable standard—any proportion above this figure being considered to be unnecessary.

The easiest method of determination is to treat two or three grms. with ether and pour off through a tared filtering crucible or filter-paper, washing the residue with ether until free from fat, drying and weighing. The residue should be examined microscopically for the presence of animal tissues, the presence of which would increase considerably the apparent amount of starch present; in those cases where such tissue is present the amount of starch should be determined chemically by acid hydrolysis, which method is reasonably accurate in the absence of pentosans and other interfering substances.

The B.P. prepared suet is directed to be the purified internal fat of the abdomen of the sheep. The characters and tests required for this are: Firm, white, unctuous. Nearly inodorous; taste bland. Saponification value 192 to 195; iodine value, 33 to 46; acid value not more than 2·0; melting-point, 45° to 50°; refractive index at 60°, 1·4490 to 1·4510 (equivalent to 1·4563 to 1·4583 at 40°).

Benzoated suet is prepared suet to which has been added 3 per cent. of benzoin in coarse powder at 60°, allowed to dissolve, strained and stirred until nearly cold.

Hen's Egg Oil

Egg oil is obtained commercially either from the dried egg yolk or from the yolk which has been coagulated by heat. The average egg (without

shell) weighs about 45 grms. of which approximately one-third is yolk. The yolk consists of about one-third fat, although Kitt obtained only 19 per cent. by extraction with ether—this would appear to be a very low result. (Cf. Parker and Paul, *Analyst*, 1910, 35, 204; Kojo, *Analyst*, 1912, 37, 25, and, particularly, Barbieri, *Analyst*, 1917, 42, 204, who states that in his opinion lecithin does not exist in egg-yolk.)

The oil has a golden-yellow colour which deposits a large quantity of stearine at ordinary temperatures. The oil is apt to become rancid and to lose its colour when exposed to atmospheric conditions. Paladino (*Analyst*, 1909, 34, 320) states that the fatty acids present consist of oleic, palmitic and stearic with a trace of formic acid, but the presence of this last acid is somewhat curious if true. The following characteristics have been observed:

TABLE CLXXXVII.—CHARACTERISTICS OF HEN'S EGG OIL

Observer.	S.G. 15°.	M.Pt. °C.	Acid Value.	Sap. Value.	Iodine Value.	Reichert.	n_D^{40}.	M.Pt. Acids. °C.	I.V. Acids.
[1] Paladino & Toso	0·914	22	..	186·0	81·4	..	..	35	..
[2] Kitt	0·914	..	1·2	190·2	82·1	0·4	..	36–39	73·2
[3] Spaeth . . .	..	..	..	184·4	68·5	0·7	1·4658	35	72·6

[1] Expressed oil. [2] Extracted with ether. [3] *Analyst*, 1896, 21, 233.

HOG FAT

(*Lard*)

Source.—At one time the name "lard" was confined exclusively to the fat obtained from the kidney bed, but it is now given indiscriminately to the fat from all parts of the hog. The preparation in America has reached enormous proportions and is done by a continuous and almost mechanical process. The animals immediately they have been slaughtered are cut up and the fat from the various parts of the animal is separated. The finest product is that produced from the kidney and bowel fat, whilst other qualities are obtained from various parts of the animal. The method of preparation is roughly very similar to that used for beef fat (page 355) the finest qualities being produced in an analogous manner to that for *première jus*, the lard so produced at a temperature not exceeding 50° from the kidney and bowels being known as "Neutral Lard No. 1" whilst a similar product prepared from the back is known as "Neutral Lard No. 2." Neutral lard is almost exclusively used in commerce either for margarine manufacture or confectioner's use.

The residues from these processes rendered at a much higher temperature are known as "leaf lard" from the kidney fat or "choice kettle rendered lard" from the back fat. These two lards, or a mixture of the two, are the usual edible lards of commerce—a lower quality known as "prime steam lard" being produced from trimmings and other parts of the animal by treatment with high-pressure steam. Lower qualities still, prepared from the viscera by treatment with caustic soda or acid, are sold as greases for commercial purposes.

Neutral lard after salting and settling is not usually refined further, it being then clear and practically free from fatty acids. The commercial qualities are refined by melting and churning up with water containing salt, in circular drums, allowing the water to settle and drawing off the fat. It is then mixed with fuller's earth and passed through filter presses. The clarified lard is then rapidly cooled on revolving drums when its transparency is lost and becomes semi-molten—it is usually allowed to set in cold storage.

Composition.—The composition of lard depends to a considerable extent on the part of the animal from which it is taken and also on the foods eaten by the animals—the more unsaturated acids occurring in some oil cakes tending to pass into the fat of the animal feeding upon them (cf. page 369). This difference in composition seems, however, to be more quantitative than qualitative, the lards of lower melting-point containing a larger proportion of unsaturated acids.

Lewkowitsch has stated that lard contains lauric, myristic, palmitic, stearic, oleic, and linolic acids, with the possible presence also of linolenic acid. Amberger and Wiesehahn (*J.S.C.I.*, 1924, 43, B229) found, however, that the fatty acids consisted of stearic, 7·8, palmitic, 32·2, and oleic, 60·0 per cent., whilst Myddleton and Barry (*Fats: Natural and Synthetic*, London, 1924, page 14) found 24·6 per cent. of palmitic, 15·0 per cent. of stearic, 50·4 per cent. of oleic, and 10·0 per cent. of linoleic. At present the presence of lower acids than palmitic must be considered to be at least doubtful and further work is desirable as lard from different animals and different parts of the same animal do vary considerably in composition, as the following results of Hehner and Mitchell (*Analyst*, 1896, 21, 326) clearly show:

TABLE CLXXXVIII.—COMPARISON OF FAT FROM VARIOUS PARTS OF HOG

Fat of Somersetshire Pig Six Months old.	Oleic Acid.	Stearic Acid.	Palmitic Acid.
From	Per cent.	Per cent.	Per cent.
Head . . .	75	9	16
Ham . . .	68·5	8·8	22·7
Breast . . .	71	11·5	17·5
Flare . . .	58·5	15	26·5
Back . . .	75	8·8	15·2

In other samples of lard they found by their own method from 6–16 per cent. of stearic acid in the mixed fatty acids.

The nature of the actual glycerides present in lard has not been fully elucidated, although a certain amount of work has been done on this problem. Already in 1896 Hehner and Mitchell (*Analyst*, 1896, 21, 328) had examined those crystals which were more insoluble in ether, and this work was continued by Kreis and Hafner (*Analyst*, 1903, 28, 359; 1904, 29, 259), who stated that they had isolated heptadecyldistearin. Later, however, Bömer (*Analyst*, 1913, 38, 204) was not able to support this and found that the insoluble glyceride is palmito-distearin and he also isolated stearodipalmitin; he was unable to isolate tristearin and concluded that it was absent. Further work along these lines is desirable as it is possible that means may be found of isolating characteristic glycerides which will help in the problem of detecting other animal fats in lard, and lard in butter

fat. Amberger and Wiesehahn (*J.S.C.I.*, 1924, 43, B229) isolated oleodistearin, oleopalmitostearin and suggest as the composition of lard, palmitosistearin, 3 per cent.; stearodipalmitin, 2 per cent.; oleodistearin, 2 per cent.; oleopalmitostearin, 11 per cent. and palmitodiolein, 82 per cent.

Analytical Constants.—The analytical constants of lard vary so much with the various factors (food part of animal, type of animal, etc.) which have been already mentioned that it will probably be more useful to take each determination by itself rather than give a table containing the somewhat wide fluctuations which have been obtained. In order to show how the constants may vary for fat from the same animals the following table compiled from various sources is appended :

TABLE CLXXXIX.—VARIATIONS IN CONSTANTS FROM SAME ANIMAL

Source.	S.G. 100°/15°.	M.Pt. Fat. °C.	M.Pt. Fatty Acid. °C.	Iodine Value. Fat.	Iodine Value. Fatty Acids.	$n_D^{40°}$.	Free Fatty Acid per cent. Oleic Acid.	
European hogs: Mean of results from 8 animals—								
Fat from back . .	0·861	33·8	40	60·6	61·9	..	..	
,, ,, kidney .	0·859	43·2	43·2	52·6	54·2	..		Spaeth
,, ,, leaf . .	0·859	44·5	42·9	53·1	53·4	..	..	
,, ,, ham . .	0·860	[1] 46	..	55·5	..	1·4588		Dennstedt & Voigtlander.[2]
American hogs: Mean of results from 3 animals—								
Fat from head . .	0·863	44·9	..	66·0	..	1·4610	..	
,, ,, back . .	0·862	47·7	..	63·9	..	1·4607	[2] Dennstedt & Voigtlander.	
,, ,, leaf . .	[6]0·863	44·5	..	61·4	..	1·4602		
,, ,, ham . .	0·863	44·5	..	67·8	..	1·4609	..	
European hogs: Mean of results from 2 animals—								
Fat from internals .	..	..	..	50·9	..	1·4577	0·3	..
,, ,, heart . .	..	..	..	55·3	..	1·4584	0·3	[4] Durier.
,, ,, back . .	..	..	..	57·0	..	1·4586	0·2	..
,, ,, head . .	..	..	..	64·5	..	1·4596	0·2	..
American hogs:								
Fat from back . .	..	12·0	21·2	93·9	104·5	1·4620	0·2	..
[3] ,, ,, leaf . .	..	20·0	22·8	93·8	108·2	1·4621	0·2	[7]Richardson
[5] ,, ,, ham .	..	15·5	20·5	93·5	109·0	1·4630	0·2	and Farey

[1] Beusemann's method.
[2] *Zeit. Angew. Chem.*, 1898, 12, 857.
[3] Mean of 3 samples.
[4] *Ann. des. falsific.*, 1909, 12, 491.
[5] Mean of 2 samples.
[6] Mean of 2 results, the third was 0·870.
[7] *J. Amer. C.S.*, 1908, 30, 1191. Abnormal lard from " oily " hogs.

Specific Gravity.—The specific gravity is not of much value in the examination of lard as the variations that have been found among genuine lards is nearly as great as the difference between the specific gravity of an average sample and that of many possible adulterants. It may, however, offer some assistance when taken in connection with other constants so that the following table may be found useful on occasion. It should always be remembered that lards with a specific gravity as high as 0·870 have been recorded.

TABLE CXC.—SPECIFIC GRAVITIES OF LARD AND OTHER FATS

Fat.	S.G. 100°/15°.	37·8°/37·8°.	Observer.
Lard	0·859–0·862	..	Parry
Lard	0·860–0·861	0·905–0·907	Allen
Lard stearine	0·857–0·858	..	Parry
Cotton-seed oil	0·868–0·872	..	Allen
Cotton-seed stearine	0·866	0·911–0·912	Allen, Parry
Beef stearine	0·857	..	Pattinson
Arachis oil	0·867	..	Allen
Coconut oil	0·874	0·910–0·916	Allen, Moore

Melting and Solidifying-Points.—The melting and solidifying-points vary considerably with the part of the animal from which the fat is taken, so that as in the case of the specific gravity these factors can only be used for comparison with other values. It is, of course, quite easy by the use of lard oil or lard stearine to prepare lards having a wide range of melting-points and the same remarks, of course, apply to the use of beef stearine. The melting-point which is given as such is that temperature at which the lard becomes perfectly transparent, but the process of melting extends over a large number of degrees (upwards of ten in some cases) from the stage at which it first commences to soften. The capillary-tube method is as accurate as any method but, of course, any of the usual methods may be used, that of Knapp, page 97, being rapid and convenient.

The solidification-point may be taken in the same way as the titre test for the fatty acids.

TABLE CXCI.—MELTING AND SOLIDIFYING-POINTS OF LARD

Melting-Point.		Solidifying-Point.		Observer.
Lard. °C.	Fatty Acids. °C.	Lard. °C.	Fatty Acids. °C.	
36–48	..	..	36–42	Fryer and Weston
30–45	37–46	..	39–42	Mitchell
..	..	24–36	..	Goske
41–49	..	..	41–42	Lewkowitsch
34–44	..	..	..	Spaeth
..	35–47	..	34–42	Various
40–47	42–45	..	..	Parry
36–40·5	43–44	27–30	41–42	Leach

The manner in which the melting-point varies with the part of the animal from which the fat is taken and with the other constants may be seen from the table on page 361.

Saponification Value.—The saponification value of lard usually falls between the limits 195–200, although somewhat higher values have been observed occasionally; the average value is about 196–197. This factor is not of any great value as rape oil is the only one which would greatly affect this constant and it is an unusual adulterant. There are occasions, however, when it should be performed.

Iodine Value.—At one time the iodine value was the most important constant in the examination of lard and frequently the presence or absence of vegetable oils could be decided on this factor alone, but changes in the food which is given to the animals have produced considerable differences in the composition of the fat and, although the test is still of importance and must not be overlooked in any doubtful case—in fact it may be looked upon almost as a routine test for lard—yet the indications obtained must be regarded with suspicion and carefully interpreted in comparison with those obtained from other constants.*

The iodine value will depend to a considerable extent upon the part of the animal from which the fat is taken, the softer lards having a higher iodine value on account of the larger percentage of oleic acid contained in these.

The iodine value of an average commercial lard usually varies between about 56 and 64, although figures both slightly higher and lower than these figures are quite common in normal lards. Any lard which gives an iodine value outside the limits 50–68 must be considered as somewhat abnormal, and further examination should be made. In this respect lards of American origin usually give higher iodine values than those of European origin, whilst the iodine value of leaf lard or of lard obtained from animals fed on coconut products may fall to 45 or even in extreme cases to below 40.

The iodine value of the liquid fatty acids may also give additional information, although it is doubtful whether the information so obtained repays the trouble involved in the separation of the fatty acids. The usual variations found for this constant are from 92–105, but Lewkowitsch has found " oily " hogs giving a value as high as 115, whilst Farnsteiner has found (*vide infra*), certain samples of Chinese and Japanese lard to give very much higher results. Any sample giving a figure of more than 105 is somewhat abnormal and one with a figure of 110 or more, distinctly suspicious, with due regard, of course, to the reservations already mentioned and the figures contained in the various tables in this section.

Refractive Index.—The usual variations for this figure at 40° are from 1·4590–1·4610 although, as will be seen from the tables given elsewhere in this section, genuine samples may give figures lying outside these figures. This figure varies with the other factors, particularly with the iodine value. Figures as high as 1·4643 have been found by Farnsteiner in Chinese and Japanese lards.

Properties and Special Tests.—Lard has few special properties or tests by which it may be found in admixture with other oils and fats. The amount of stearic acid present is not sufficient to distinguish it from other fats, and the only test likely to be of service is the microscopic and chemical examination of the glycerides least soluble in ether for the detection of adulteration in lard itself—it is possible that this might be extended to the detection of lard in other substances.

* *J.S.C.I.*, 1893, **12**, 470.

At one time lard was supposed to be entirely free from the fat soluble vitamin A, but more recently it has been found that certain samples contain appreciable quantities (*J.S.C.I.*, 1920, 39, 609A; 1921, 40, 81T; 1923, 42, 509T. *Analyst*, 1924, 49, 98.) The deficiency has been shown to be due to the lack of the substance in the diet of the animals and destruction during commercial preparation. (*Analyst*, 1921, 46, 244; 1923, 48, 130). The detection of the fat of other animals, such as beef and mutton fat, in lard is difficult. In some cases it would certainly be possible to find an admixture of 10 per cent. of beef stearine, but in other cases this amount might pass undetected, whilst, on the other hand, some samples of pure hog fat show characteristics which are distinctly suspicious. (Cf. *Analyst*, 1925, 50, 511.)

The first work on the subject was carried out by Husson in 1878, and on this work the well-known test of Belfield was based. In the original method 40 drops of melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool, the test-tube is closed with cotton-wool and allowed to stand in a cool place until crystallisation commences. In the event of immediate crystallisation a larger quantity of ether should be used. The crystals so obtained are examined microscopically. The crystals from pure lard are usually flat oblong plates with chisel-shaped ends, whilst those from beef (or mutton) fat form tufts of thin needles radiating from a point. It has been shown by Dunlop (*J.S.C.I.*, 1906, 25, 459) that repeated crystallisation from ether converts the crystals of beef fat into flat crystals like those of lard.

The method was studied by Stock (*Analyst*, 1894, 19, 2) who attempted to place the method on a quantitative basis. Stock prepared two standard sets of mixtures, one with a lard of M.Pt. 34°–35° containing 5, 10 and 15 per cent. of beef stearine, M.Pt. 56° and the other set with a lard melting at 39°–40° with the same proportions of beef stearine melting at 50°. For the determination he took the melting-point (by the capillary-tube method) of the lard and then compared it by the following test with that standard mixture to which its melting-point most nearly approximated: Place 3 c.c. of the melted fat, measured in a pipette, in a stoppered 25 c.c. graduated cylinder and dissolve in 21 c.c. of ether. Allow to stand at 13° for 24 hours—after which time, measure the volume of crystals produced and examine their appearance under the microscope. Stock determined the proportion of adulterant by weighing the amount of washed ether deposit. The ether from each cylinder is poured off as far as possible and 10 c.c. of fresh ether cooled to 13° added. The contents of the cylinders are well mixed, allowed to stand, and the ether poured off as before. This operation is repeated, the crystals are then washed into a weighed beaker, using the ether previously poured off, the ether carefully drained off and the remaining crystals dried at 40° for fifteen minutes and weighed. The amount of crystals obtained will depend upon the melting-point of the lard. Observations by Stock, Dunlop (*J.S.C.I.*, 1906, 25, 458) and Lewkowitsch show that the weight varies from not more than 10 milligrams with lards melting up to about 40° (melted to a clear liquid) to as much as 190 milligrams in the case of a lard melting at 50°. A sample of beef stearine gave 1·5 grms. of deposit when examined by the same process.

It may be difficult to determine with certainty the addition of a small amount of adulteration to a hard lard but the Stock method is one which is likely to be of assistance. The indications obtained should be looked upon with suspicion and a conclusion drawn only after a most thorough experience has been obtained with various lards and admixtures. One point should be carefully remembered as the basis of this test. Beef is considerably more insoluble in ether than lard and the crystals obtained

[*By permission of J. & A. Churchill*

FIG. 8.—Photomicrographs of Lard and Beef Crystals
(E. R. Bolton)

1. Beef-fat (polarised light) × 150. 2. Beef-fat (polarised light) × 70.
3. Beef-fat × 150.
4. Lard × 250. 5. Lard × 150

have, in general, a different microscopic appearance consequent upon the variation in the composition of the glycerides.

Emery (*U.S. Dept. of Agri.*, 1908, *Circular* 132·1) bases a method for the detection of beef fat upon the M.Pts. of the crystals obtained by crystallisation and recrystallisation of the fat from ether. The following table is taken from his results:

TABLE CXCII.—DETECTION OF BEEF FAT IN LARD (EMERY)

Fat.	M.Pt. °C.	Fat.	M.Pt. °C.
Pure lard	63·8	Lard containing 8% beef fat .	61·6
Lard containing 1% beef fat .	63·4	„ „ 9% „ „ .	61·6
„ „ 2% „ „ .	63·2	„ „ 10% „ „ .	61·5
„ „ 3% „ „ .	63·0	Beef fat	60·6
„ „ 4% „ „ .	62·8	Lard	63·6
„ „ 5% „ „ .	62·5	Lard and 10% lard stearine .	63·8
„ „ 6% „ „ .	62·2	„ „ 15% „ „ .	63·6
„ „ 7% „ „ .	61·6		

This method is carried out as follows: "Weigh 5 grms. of the melted fat into a glass stoppered, 25 c.c. cylinder, about 150–175 mm. in height; add warm ether up to 25 c.c. mark; stopper securely and shake until the fat is completely dissolved. Allow the cylinder to stand for about 18 hours at a temperature of 16°–20° C. during which time some of the solid glycerides will crystallise out. Decant the clear solution carefully from the crystals, wash with three 5 c.c. portions of cold ether, avoiding breaking up the deposit during the first two washings. Agitate the crystals with a third portion of ether and transfer to a small filter. Wash on the paper with successive small amounts of cold ether until 15 to 20 c.c. have been used; then remove the last traces of ether by means of slight suction on the stem of the funnel. Break up any large lumps and allow the deposit to dry.

"When thoroughly dried, pulverise the glycerides and take their melting-point in a closed 1 mm. tube. Heat the water in the beaker rapidly to about 55° and maintain that temperature until the thermometer carrying the melting-point tube registers 50° to 55°. Then heat again and carry the temperature of the outer bath somewhat rapidly to 67°, when the flame is removed. The melting-point of the crystals is regarded as that point when the fused substance becomes perfectly clear and transparent. A dark background placed about 4 inches from the apparatus will prove of advantage. When the melting-point of glycerides obtained by this method is below 63·4° the presence of beef fat should be suspected, while a melting-point of 63° or below, can be regarded as positive evidence that the sample is not pure lard. It is advisable to carry out this method with a control sample of lard in connection with each batch of samples analysed."

Many more samples would have to be examined before this can be taken as of definite value but it is possible that the melting-point of such crystals after mixing with similar crystals obtained from pure lard and pure beef fat respectively might show, by the depression of the melting-point caused by the addition of the dissimilar crystals, useful results. The method

has been very favourably considered by the American *A.O.A.C.* by whom this method has now been made official. (*J.A.O.A.C.*, 1915, 1, 183, 515.)

A method depending upon the difference between the melting-point and the solidifying-point has been devised by Polenske (*Analyst*, 1907, 32, 382; 1908, 33, 476). This " difference value," although fairly constant for each individual fat, varies considerably between different kinds. The melting-point is taken as that point at which the fat becomes perfectly clear—the solidifying-point is determined by observing the point at which two marks on the cooling test-tube become invisible when kept continually stirred. Polenske recommends the column of fat to be 2·7 cm. high and 1·8 cm. in diameter. Lard was found to give a " difference value " of about 20, whilst beef fat gave a " difference value " of about 13°. Polenske considered that all lards showing a " difference value " of less than 18·5° were adulterated. The method has been favourably commented upon by Laband (*Analyst*, 1909, 34, 525) and not very favourably by Fischer and Wewerinke (*Analyst*, 1914, 39, 216). The theoretical basis of the test is discussed by Bömer and Limprich (*Analyst*, 1913, 38, 204), who show that the palmito-distearin of lard shows a value of 18·4° whereas the palmito-distearin of beef and mutton fat has a value of 11·8°. They state that the method is capable of detecting about 20 per cent. of beef fat and 15 per cent. of mutton fat in lard. They further state that the melting-point should not be taken until many hours have elapsed since the fat solidified.

A method due to Bömer and his co-workers (*Analyst*, 1914, 39, 84, 171) depends upon another property of the same glycerides, the difference between the melting-point of the glycerides and that of the fatty acids contained therein. The palmito-distearin of lard gives a difference of 5·2°, whilst the palmito-distearin of beef gives a difference of 0·1°. The test is carried out as follows : Place about 50 grms. of the molten fat in a 150 c.c. CO_2 flask and add 50 c.c. of ether, mix thoroughly, cork the flask, and allow to stand at a temperature of about 15° until crystallisation has ceased, which requires several hours. Shake the mixture thoroughly and pour on to a Buchner funnel about 9 cm. in diameter and filter with the aid of a light suction. The crystals are pressed between filter-paper, returned to a similar flask, melted and dissolved in 50 c.c. of ether and again allowed to crystallise, filtering as before. A portion of the resulting glycerides are retained so that their M.Pt. may be determined and the fatty acids are prepared from the remainder in the usual way (page 44). Bömer states that with glycerides of M.Pt. between 60° and 61° beef fat is indicated if the difference is less than 5·0°, whilst in the case of glycerides of M.Pt. of 65°–68·5° beef fat is indicated where the difference is less than 3·0°. Vegetable oils do not interfere but vegetable fats may be mistaken for beef fat by this test as also might hydrogenated oils, but the phytosteryl acetate test will be of assistance here.

The test was not commented upon very favourably by Fischer and Wewerinke (*Analyst*, 1914, 39, 216), who stated that it was no more sensitive than that of Polenske although more rapid and convenient. Sprinkmeyer and Diedrichs, however (*Analyst*, 1914, 39, 253), state that they can always find 10 per cent. of beef fat and nearly always as little as 5 per cent. They found the difference in the case of lard to be from 4·4°–7·4°, whilst that in the case of beef and mutton fats was 0·8°–1·2°. They propose the value MG+2*d* which is the M.Pt. of the glyceride+twice the difference. For lard this is 73·1–76·5 and for beef or mutton 65·2–67·3. Mixtures of lard with 5 to 10 per cent. of beef gave as this new factor a figure always below 72 and usually below 70. Bömer (*J.S.C.I.*, 1922, 41, 431A) has continued this work and has found that lard always gives a value for MG+2*d* well

above 71 and considers that any lard which gives a figure of 71 or less is adulterated. This test, taken in conjunction with the Belfield-Stock method, is undoubtedly the best means that we have at the moment for detecting foreign animal fats in lard. The methods of Polenske and Bömer have been critically examined by Prescher, who states that the Bömer method is extremely useful and is much to be preferred to that of Polenske.

Somewhat similar methods have been proposed by Vitoux and Muttelet (*Analyst*, 1921, 46, 94) and by Kerr (*J.S.C.I.*, 1921, 40, 159A).

Wesson and Lane (*J.S.C.I.*, 1905, 24, 714) have proposed the use of a test, depending upon the titre value of the sample, for mixtures of beef stearine with cotton-seed oil.

Examination for Adulteration.—One of the commonest forms of adulteration is the addition of water. Lard should contain at least 99 per cent. of fat and in the usual commercial condition contains not more than 0·5 per cent. of moisture. The water may be determined as under butter, page 432. The determination of small quantities of water in lard is discussed by Polenske (*Analyst*, 1911, 36, 497), who uses the following method : The semi-liquid lard is placed in a test-tube fitted with a cork carrying a thermometer and heated to a temperature of 52° by immersing the test-tube in a water-bath; the tube is then removed from the bath and shaken until the temperature falls to 40°; if the lard is clear at 52°, and does not become turbid at 40° it contains less than 0·15 per cent. of water. Should it become turbid at 40° its water-content lies between 0·15 and 0·2 per cent. If turbid at 52° the lard is heated to 95°; a turbidity at this temperature indicates the presence of more than 0·45 per cent. of water. Should the lard be clear at 95°, it is gradually cooled until a turbidity appears, the quantity of water present being then ascertained by reference to the following table :

TABLE CXCIII.—TURBIDITY OF LARDS

Water Content.	Temperature at which Lard becomes turbid.
Per cent.	°C.
0·45	95·0
0·40	90·8
0·35	85·0
0·30	75·2
0·25	64·5
0·20	53·0

Of course, if the lard is not clear at these temperatures it should be ascertained whether the turbidity is actually due to the presence of water.

Paraffin wax has been used as an adulterant in fairly large quantities but this is no longer practised. Small amounts have been added to lards and lard mixtures with the object possibly of interfering with the phytosterol acetate test (q.v.) for vegetable oils and for stiffening purposes. Tests for its detection have been proposed by Polenske (*Analyst*, 1906, 31, 46), Shrewsbury (*Analyst*, 1909, 34, 348), Dunlop (*Analyst*, 1909, 34, 524), and Thompson and Hurst (*Chem. News*, 1910, 102, 109). That due to Shrewsbury is probably as delicate as any, it is performed as follows :

Five grms. of the melted lard are measured in a cylinder, transferred to a 300 c.c. Reichert flask, and saponified with 20 c.c. of glycerol soda, made by mixing 100 c.c. of approximately 10N/NaOH (453 grms. soda and 1000 c.c. water) with 500 c.c. of glycerol. The hot mass is dissolved in

50 c.c. of industrial (non-mineralised) methylated spirits, added very gently, drop by drop, from a pipette. The solution is allowed to cool, and its appearance observed when cold. If it is clear, paraffin wax is absent. As little as 2 per cent. of paraffin wax makes the solution cloudy with opaque flocculi. After some time the solution sets to a jelly, when it may be again observed. Genuine lard gives a slightly opalescent but homogeneous jelly.

Two per cent. of paraffin wax shows many opaque flocculi distributed throughout the otherwise nearly transparent jelly, and gives a very characteristic cloudy appearance.

Some confusion arose in foreign journals over the use of methylated spirits (cf. *J.S.C.I.*, 1913, 32, 1118) but the matter was subsequently corrected by Shrewsbury (*Analyst*, 1914, 39, 43, 296). The detection of paraffin is further discussed under phytosteryl acetate (page 125).

The main adulteration is either the admixture or the complete substitution of foreign oils. For this purpose the oils which have been most commonly used are coconut and palm kernel, cotton-seed, arachis, maize and sesamé oils, and tallow.

The methods for the detection of tallow have already been discussed. Coconut and palm-kernel oils are detected by means of the Reichert-Polenske value. The average values for lard are 0·3 for the Reichert and 0·3 for the Polenske. Where these numbers are seriously exceeded the amount of the foreign oil may be determined by the methods given on pages 334, etc., using the table for margarine and coconut oil without butter fat; due regard should also be paid to the methods of distinguishing between coconut oil and the other oils of like character there suggested.

Cotton-seed oil may be detected by the Halphen test (q.v.) due regard being paid to the fact that this oil may be treated so that it no longer gives the reaction and also that the fat from animals fed on cotton-seed cake may give reactions, corresponding to 1 or 2 per cent. of the oil. The iodine value will be raised if appreciable quantities of vegetable oils are present. The sulphur-chloride test may also be used with advantage. Sesamé oil may be detected by the Baudouin reaction, but here again slight indications should be disregarded for similar reasons. Maize oil will be indicated by the increase in the iodine value and the decrease in the solidifying-point of the fatty acids (M'Pherson and Ruth, *Analyst*, 1907, 32, 329). Arachis oil cannot be detected by Evers's qualitative test, but the quantitative method may be used providing that the arachidic acid be recrystallised until its M.Pt. is at least 70°.

In all cases where vegetable oils are suspected either from the iodine value or from colour tests the phytosteryl acetate should be performed and the indications obtained therefrom carefully interpretated in the light of the other tests. Maize oil has been suggested as a likely adulterant of lard. M'Pherson and Ruth (*Analyst*, 1907, 32, 329) state that as little as 2 per cent. may be detected by the phytosteryl acetate test, but in view of the complicated nature of the sterols of maize oil this would appear to be unlikely (cf. under maize oil, page 205). The detection of japan tallow in lard is mentioned on page 288 under japan tallow.

As has already been noticed some samples of Chinese and Japanese lards have given some rather extraordinary results. Thus the following figures have been obtained by Farnsteiner :

n_D^{40} 1·4593 to 1·4642; iodine value of the fat 58–101·7; iodine value of liquid fatty acids 111–138·7.

Rae has published the following figures for Ceylon lard (*Analyst*, 1924, 49, 84) :

Specific gravity 99°/15°, 0·8851; butyro-refractometer reading at 40°,

52·0; acid value, 11·12; saponification value, 216·4; iodine value (Wijs), 44·8; unsaponifiable matter, per cent. 0·40.

The Effect of the Diet of the Animal on the Composition of the Fat.—The composition of lard depends within certain limits on the food of which the animal has partaken; thus Lewkowitsch has pointed out that hogs fed exclusively on acorns yield a harder lard than hogs fed on maize. In general where the animals are fed on fatty foods the composition of the lard tends to change in the direction of the composition of the oil used as food. Thus Gibbs and Agcaoili (*Phil. J. of Science,* 1910, 11, 33) have shown that the use of copra lowers the iodine value and the refractive index and raises the saponification value. It is possible that such lards will contain acids of lower molecular weight than palmitic (cf. composition, page 360). When vegetable oils or oil-cakes are used the lard becomes softer and the iodine value higher and, moreover, the substances which cause the characteristic colour tests of sesamé and cotton-seed oil tend to pass into the lard. König and Schluckebier have shown that the lard from hogs fed on sesamé cake (*Z. f. Unters. d. Nahrgs. u. Genussm.*, 1908, 15, 648) give the Baudouin reaction. Many observers have shown that the lard from animals fed on cotton-seed cake give the Halphen reaction. Langfurth (*Z. f. ang. Chem.*, 1901, 15, 685), Fulmer (*J.A.C.S.*, 1902, 24, 1148; 1904, 26, 837), Dunlop (*J.S.C.I.*, 1906, 25, 458). The indications thus obtained from the colour test would not, as a rule, point to more than 10 per cent. of cotton-seed oil, although larger amounts than this have been obtained in the case of individual animals. It has been shown by Tolman (*J.S.C.I.*, 1905, 24, 692), however, that those lards which of themselves give a positive result in the Halphen reaction do not contain phytosterol. Bengtsson (*Analyst*, 1923, 48, 225) has examined the fats of hogs which had been fed on Babassu cake up to 1 kilo per day and found that the iodine value was decreased by several units, the refractive index was lowered slightly and the M.Pt. was raised one or two degrees. Martin (*Analyst*, 1923, 48, 387) found that when fish meal formed from 11–14 per cent. of the diet the lard was free from fishy odour and had normal characteristics—a trace of octobromstearic acid was found, however, by the method for fish oils (*A.O.A.C.*).

A report has been made by Willcox and Cranfield (*Analyst*, 1925, 50, 324) on the influence of palm-kernel meal on the composition of bacon fat. Four pens of six pigs each were fed on the following rations :

	Pen 1. Per cent.	Pen. 2. Per cent.	Pen 3. Per cent.	Pen 4. Per cent.
Ration for first six weeks—				
Palm-kernel cake meal . .	20	..	40	..
„ meal (extracted)	..	..	..	40
Sharps	70	70	50	50
Barley meal	10	10	10	10
Bean meal	..	20	..	..
Whey	One gallon per pig per day to all pens			
Ration for last six weeks—				
Palm-kernel cake meal . .	20	..	40	..
„ meal (extracted)	..	..	..	40
Sharps	20	20	10	10
Barley meal	60	60	50	50
Bean meal	..	20	..	..
Whey	Two gallons per pig per day to all pens			

The age of the pigs at the outset was sixteen weeks. At the end of the twelve weeks' period the pigs were sold to a well-known firm of pork butchers and bacon curers, who gave an expert opinion on the pork from the merchant's point of view. They stated : " For a porker or cutting pig you could not find any difference in any of the pigs."

The most suitable bacon pig was selected from each pen and cured for bacon. The curers reported on the bacon as follows :

Pen 1. (Receiving 20 per cent. of palm-kernel meal, containing 6 per cent. of oil.) " Soft in the fat."

Pen 2. (Receiving no palm-kernel meal.) " Fat firm and the best of the lot."

Pen 3. (Receiving 40 per cent. of palm-kernel meal, containing 6 per cent. of oil.) " Softer than No. 2, and will, no doubt, be very soft and tallowy in one or two months."

Pen 4. (Receiving 40 per cent. of palm-kernel meal, 1½ per cent. of oil.) " Soft but not so bad as Nos. 1 and 3."

From these comments it appears that the palm-kernel meal had some influence on the consistence of the bacon fat, tending to make it soft.

Samples of the back bacon fat were taken for analysis. Two methods of extraction of the pure fat were used : (*a*) The crude fat was cut into thin strips and rendered at a temperature not exceeding 70 C.; (*b*) the crude fat was passed through a mincing-machine and then extracted with petroleum spirit in a Soxhlet extractor. The samples of pure fat gave the following results on analysis :

TABLE CXCIV.—COMPARISON OF FATS FROM HOGS FED ON VARIOUS DIETS

	From Pen No.	Iodine Value.	Sapon. Value.	M.Pt. °C.	R.M. Value.	Polenske Value.	Zeiss Butyro-refractometer No. at 40° C.
(*a*) Rendered fat.	1	56·5	205·8	29·5	0·44	0·6	48·5
	2	59·7	198·0	28·0	0·49	0·9	48·5
	3	57·2	198·5	29·0	0·55	0·6	48·0
	4	56·1	200·5	29·0	0·44	0·6	38·0
(*b*) Fat extracted with petroleum spirit	1	56·5	199·5	30·0	0·60	0·7	48·5
	2	56·1	193·4	28·0	0·66	0·7	49·5
	3	56·8	197·9	30·0	0·44	0·7	48·0
	4	58·6	202·3	30·5	0·55	0·7	48·5

Willcox and Cranfield state that the only indications of possible influence due to palm-kernel feeding are a slight rise in the saponification value and also in the melting-point. These, however, do not follow the increase in palm-kernel oil given in the rations, since the highest saponification value figures (*a*1 and *b*4) and the highest melting-points (*a*1 and *b*4) are not from the pen receiving the largest amount of palm-kernel oil (*a*3 and *b*3).

Judging from these figures, one must arrive at the conclusion that the analytical data do not explain the experts' comments on the quality of the bacon and consistence of the fat.

Lard Substitutes.—These usually consist of lard stearine together with beef stearine, cotton-seed oil and stearine and other vegetable oils or, on the other hand, they may be entirely free from lard or lard stearine. They are prepared by mixing the fats together in a mixing machine—the actual composition depending upon the country in which the product is to be used

and the season of the year—and pouring the mixture on to cooling drums as in the case of lard.

As lard contains practically no water it would seem natural to expect that a lard substitute would also be practically free. Quite a number of such products have, however, contained considerable quantities of water, which may be determined as under butter, but this should be looked upon as adulteration.

Lard Oil; Lard Stearine.—The separation of lard into oleine and stearine is carried out in a similar manner to the same operation in the case of beef. It is necessary, so that good separation may be affected, for the lard to be carefully crystallised. The crystallised lard is then wrapped in cloths and the oleine—lard oil—removed by pressure, the finest qualities being prepared in lever presses worked by hand. Lard stearine is used in the manufacture of lard substitutes, for increasing the consistency of soft lard and in the manufacture of margarine and cooking fats; inferior qualities are used in the manufacture of candles. Lard oil is used as a lubricant and for burning. The following are average values for the various characteristics, but it follows from the method of preparation that these may be subject to considerable variation:

	S.G. 100°/15°.	Sap. Value.	Iodine Value.	Refractive Index. 40°.
Oil . . .	0·863	192	80	1·4607
Stearine . .	0·858	195	50	1·4582

Horse Fat

Horse fat is not infrequently an article of commerce. It is prepared along the same lines as animal tallow, but is frequently of a lower grade for obvious reasons. Samples of genuine horse fat, rendered by himself, were examined by H. Dunlop (*Analyst*, 1907, 32, 317), his results are given in the following table:

Table CXCV.—Examination of Horse Fat (Dunlop)

	Colour and Consistence.	Iodine Value.	n^{40}.	Sap. Value. %	Unsap. Matter. %	S.G. 15·5°.	Free Acid.	R.W. No.
Horse fat from belly	Orange yellow, butter-like	85·66	1·4604	19·84	0·54	..	8·80	..
Horse fat from neck " mane "	Light yellow, part liquid	86·70	1·4612	19·91	..	..	0·56	..
Horse oil after filtration at 12·2 C.	Lemon yellow, oil	90·10	1·4616	..	0·46	0·9182	..	0·30
Horse fat from neck (" mane ")	Light yellow, part liquid	90·07	1·4612	..	..	..	..	..
Horse oil after filtration at 8·9 C.	Lemon yellow, oil	93·11	1·4616	19·56	0·50	0·9184	1·20	0·2
Horse fat from kidney bed	Orange yellow, part liquid	110·65	1·4643	..	..	..	..	..
Horse oil after filtration at 13·3 C.	Orange yellow, oil	114·85	1·4647	19·63	0·68	0·9212	..	0·35
Horse oil from neck fat	Lemon yellow, oil	112·85	1·4643	19·63	0·42	1·9211	0·46	..

Quite different results were, however, obtained for the kidney fat of a horse 15 years old by Raffo and Foresti (*ibid.*, 1910, 35, 68) who found

Saponification value . . .	196·7
Iodine value	77·3
Reichert value	1·1
Melting-point, °C. . . .	31·5°

Klimont, Meissl and Mayer in an examination of four samples of fat (*J.S.C.I.*, 1915, 34, 668) found characteristics as given in the following table in which are included also figures obtained by Heiduschka and Steinruck (*ibid.*, 1921, 40, 665A):

Table CXCVI.—Examination of Horse Fats (Klimont, Meish and Mayer: Heiduschka and Steinruck)

	Klimont, Meish and Mayer.	Heiduschka and Steinruck.
Specific gravity, 15° . .	0·937–0·946	0·922
Iodine value	74·9–78·1	75·2
Acid value	1·4–2·9	2·6
Saponification value . .	193·1–200·4	203·9
Melting-point, °C. . .	20–41	32·3

The former authors found the liquid acids to consist of oleic, linolic and linoleic acids, whilst heptadecylic acid was stated to be found among the solid acids; the latter authors state that the mixed fatty acids consist of linolenic acid, 1·7, linolic acid, 6·7, oleic, 55·2, stearic, 6·8, and palmitic, 29·5 per cent. respectively, whilst the unsaponifiable matter amounted to 0·43 per cent.

Neat's-Foot Oil

Neat's-foot oil in its general significance is obtained from the feet of cattle by boiling with water after hair, skin and hoofs have been removed, when the oil rises to the surface and may be skimmed off. The oil is purified by salting, washing with water and filtering while hot. In many cases the lower part of the leg is included in the raw material used in the preparation of neat's-foot oil especially in America—this will tend to raise the melting-point of the product.

Years ago, particularly in England, the preparation of neat's-foot oil was carried out on a small scale in local establishments, but more recently, particularly in America, the preparation of this and similar products is becoming more a question of large establishments, with consequent disappearance of the older order.

The composition of the oil is apparently quite simple. Coste and Shelbourn (1903, 22, 775) found that the acids consisted chiefly of oleic (no acids were present more unsaturated than this) with some palmitic and stearic. Eckart (*Analyst*, 1922, 47, 521) found in the oil 2 to 3 per cent. of stearic acid, 17 to 18 per cent. of palmitic acid and 74·5–76·5 per cent. of oleic acid.

TABLE CXCVII.—CHARACTERISTICS OF NEAT'S-FOOT OIL

Authority.	S.G. Value.	Sap. Value.	Iodine Value.	Reichert.	n_D^{40}.	Acid Value.	Titre. °C.	I.V. Acids.	Unsap. per cent.
Dunlop . .	0·916	197·0	71·8–74·1	..	1·4600	..	..	..	..
Coste and Shelbourn	0·915–0·918	193·6 199·7	66·4 73·1	0·9–1·2	1·4605 1·4616	..	24–28	71·0–77·0	0·12 0·65
Gill and Rowe .	0·914–0·919	..	67·1–72·9	..	..	..	..	63·6–69·5	..
Lythgoe . . .	0·913–0·915	..	71·3–73·0	..	1·4608–1·4610	..	..	..	..
Holde & Stange.	..	196–199	66–74	..	..	..	..	..	..
Fahrion . .	..	190–198	65–78	..	..	Not above 6	..	..	..
Bruno . . .	0·917	194	75·3	..	1·4595	1·7	..	..	..
Eckart . . .	[6]0·903–0·905	191·8 196·2	57·4–72·3	0·4	..	0·1–6·3	..	..	..

[1] *Analyst*, 1907, 32, 317.
[2] *J.S.C.I.*, 1903, 22, 775.
[3] *J.S.C.I.*, 1911, 30, 818.
[4] *Analyst*, 1921, 46, 371.
[5] *Analyst*, 1922, 47, 521.
[6] At 50°/50°. Sol. Pt. 4 to −2.

In regard to the adulteration of neat's-foot oil the following remarks of Fahrion (*J.S.C.I.*, 1911, 30, 818) will be of interest:

"Neat's-foot oil, in spite of its high price, is the oil most frequently used in the manufacture of chrome leather. The reason for this lies in its great resistence to oxidation and rancidity and the somewhat low temperature at which it solidifies. The admixture with it of oil extracted from the feet of sheep and pigs or the hoofs of horses can hardly be counted as adulteration, as all these oils have a similar composition. The same applies to bone oil which is frequently added after a process of refining by which the dirt, free fatty acids and most of the glycerides are removed. Real adulterations consist of additions of vegetable oils, principally rape and cotton-seed oil."

The original neat's-foot oil was originally prepared purely from the feet, so that in the most restricted sense the oil from any other source is adulteration, but the use of the feet of other animals giving an equally satisfactory oil seems now to be generally accepted and is, therefore, possibly not objectionable.

Neat's-foot oil has been adulterated in many ways. Bone oil, fish oils

and seed oils have been extensively used. For the detection of adulteration the solidifying-point, iodine value, unsaponifiable matter and insoluble bromide test are most likely to lead to useful results. The mineral matter of bone oil is frequently high, so that a determination of the ash might lead to the detection of this substance. The acid value of the oil should be low, whilst practically no precipitate should be obtained in the insoluble bromide value. The sterol of neat's-foot oil consists entirely of cholesterol, so that the addition of vegetable oil will be detected by the phytosteryl acetate test.

Some other oils which are likely to be present in neat's-foot oil are dealt with below.

Sheep's-Foot Oil.—This oil, which was the standard oil adopted for use in Amagat and Jean's oleo-refractometer, is prepared in a similar way to neat's-foot oil; it has the following characters: *

Specific gravity 15°/15°	0·917
Solidifying-point °C.	1
Saponification value	194·5
Iodine value	74–84
Titre °C.	20–21
n_D^{40}	1·4601

The following colour reactions have been proposed by Chercheffsky (*J.S.C.I.*, 1913, 32, 542) for distinguishing ox-foot and sheep's-foot oil: " (1) 20 grms. of the oil are dissolved in 5 c.c. of carbon bisulphide, and the solution added little by little to 10 grms. of sulphuric acid (sp. gr. 1·84). Ox-foot oil gives a brownish-red colouration, whilst the liquid remains clear; sheep's-foot oil gives a yellowish-brown colouration and a turbidity. (2) 20 grms. of the oil are dissolved in 5 c.c. of carbon bisulphide, and the solution treated with 10 drops of a solution of potassium bichromate in strong sulphuric acid. Ox-foot oil gives a brown colouration and sheep's-foot oil a straw-yellow colouration. (3) A mixture of 10 c.c. of the oil, 10 c.c. of hydrochloric acid, and 0·1 c.c. of a 2 per cent. alcoholic solution of furfurol is shaken for 2 minutes. Ox-foot oil becomes brown and the colour is intensified on heating, whilst sheep's-foot oil remains colourless even when heated." As in the case of most colour reactions the results obtained must be interpreted with reserve.

Horse's-Foot Oil.—This oil is obtained in a similar manner to neat's-foot oil. It should be distinguished from horse oil, which is the liquid fat obtained from other portions of the animal. According to Lewkowitsch (*Oils, Fats and Waxes*) the oil gives several of the colour reactions usually considered as characteristic of marine animal oils, whilst Dunlop (*Analyst*, 1907, 32, 317) found that the sulphuric acid reaction was given by a sample of the kidney fat. The following constants have been observed by Lewkowitsch, Jean and Amthor, and Zinck:

Specific gravity, 15°/15°	0·920–0·927
Saponification value	195–197
Iodine value	73–90
Titre, °C.	27–28·6

Bone Fat.—This is the oil obtained from the " shin-bone " of cattle and should be distinguished from the " foot " oil, although frequently the

* Lewkowitsch (*Oils, Fats and Waxes*). Bruno (*Analyst*, 1921, 46, 371).

two are prepared together. The following characteristics have been observed:

Specific gravity 50°/50° . . .	0·901–0·903
Melting-point °C.	44–45
Solidifying-point °C. . . .	32·6–33·8
Acid value	0·3–9·0
Saponification value	186·7–196·1
Iodine value	46–79·8 *
M.Pt. fatty acids °C. . . .	40–44

Fahrion (*Analyst*, 1911, 36, 512) obtained figures as low as 13° for the M.Pt. of the fatty acids of bone oil, whilst other observers have obtained widely fluctuating figures under various conditions, and from bones from various parts of the body. (Cf. Eckart, *Analyst*, 1922, 47, 521; Kraus, *J.S.C.I.*, 1918, 37, 104A.)

* More usually 50 – 60.

CHAPTER XXV

MILK FATS

Butter Fat

Source.—The source of butter fat will be sufficiently discussed later; it may be mentioned here, however, that the fats from the milk of other animals, besides that of the cow, are converted into the corresponding "butters" in some countries, details of which will be found under ghee, Samna, etc., on page 401.

Composition.—The fatty acids which have been found in butter with certainty are butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic and oleic.

Wein claims to have discovered both formic and acetic acid in fresh butter, but the methods adopted by him are open to some objection, and as his statement has never been confirmed by subsequent investigators it must be stated that their presence has still to be proved. Their presence in rancid butter is, however, quite possible, but even this has not been definitely decided.

The presence of butyric acid is the great point in its composition which distinguishes butter fat from almost all other known fats (for a list of those containing acids of low molecular weight see the Reichert value, page 151), whilst in addition to butter fat, only oils of the coconut family contain notable amounts of caproic, caprylic or capric acids. As these acids are all more or less soluble in water and volatile with steam, butter fat is distinguished by the considerable proportions of soluble acids which it contains.

The first serious quantitative examinations of butter fat were made by Duclaux (*C.R.*, 1886, 1022) and, somewhat later, by Violette (*J.S.C.I.*, 1890, 9, 1157). Although now only of historical interest the results obtained by Violette are given in the following table, the second place of decimals being, for obvious reasons, omitted:

Table CXCVIII.—Examination of Butter (Violette)

	1.	2.	3.	4.	5.	6.	7.	8.
	%	%	%	%	%	%	%	%
Butyrin	6·9	6·1	6·3	5·8	5·3	5·5	5·5	5·0
Caproin	4·1	3·6	3·7	3·4	3·1	3·2	3·1	2·9
Glycerides of insoluble volatile acids . . .	3·1	3·2	3·0	3·2	3·1	2·5	3·2	3·2
Glycerides of non-volatile acids	86·0	86·6	86·6	86·9	88·1	88·1	87·6	88·4

Other workers dealing with the problem at about the same time were Bell, Blyth and Spallanzani, from whose work the following results have been obtained by Lewkowitsch:

TABLE CXCIX.—EXAMINATION OF BUTTER (LEWKOWITSCH)

	Bell.	Blyth.	Spallanzani.
	Per cent.	Per cent.	Per cent.
Butyrin	7·01	7·7	5·08
Caproin	2·28	0·1	1·02
Caprylin and caprin	..	..	0·31
Olein	37·73	42·2	93·59
Palmitin, stearin, etc.	52·98	50·0	..

Keofoed (*Analyst*, 1892, 17, 130), working with a sample of Dutch butter, found that the fatty acids consisted of butyric acid, 1·5; caproic acid, 2·0; caprylic acid, 0·5; capric acid, 2·0; lauric acid, 8·0; myristic acid, 22·0; palmitic acid, 28·0; stearic acid, 2·0; together with oleic acid and acids of the formulæ $C_{15}H_{28}O_4$ and $C_{29}H_{54}O_5$, 34 per cent. Browne, by more detailed work arrived at the following composition for the butter with which he was working (*J. Amer. C.S.*, 1899, 21, 612, 807, 975).

TABLE CC.—PERCENTAGE OF TRIGLYCERIDES IN FATTY ACIDS OF BUTTER

Acid.	Percentage of Acid.	Percentage of Triglycerides.
Butyric	5·45	6·23
Caproic	2·09	2·32
Caprylic	0·49	0·53
Capric	0·32	0·34
Lauric	2·57	2·73
Myristic	9·89	10·44
Palmitic	38·61	40·51
Stearic	1·83	1·91
Oleic	32·50	33·95
Dioxystearic	1·00	1·04
Totals	94·75	100·00

The presence of hydroxy acids has been deduced by other observers besides Browne, such as Vachtel and Bondzynski and Rufi, but Lewkowitsch (*Oils, Fats and Waxes*, 5th, II, 802) states that such do not exist, and Crowther and Hynd (*Biochem. J.*, 1917, 11, 139) consider that any hydroxystearic acid found in the acids obtained from butter fat is to be regarded as the result of oxidation and that it is not present originally.

Of later years both of the two obvious methods of attacking the problem, namely, separation of the original glycerides, and saponification of the fat

and separation of the resulting acids, have been studied. The most success has so far come from the second method which will first be dealt with.

The problem has been studied by Jensen (*Analyst*, 1905, 30, 397), Fleischmann and Warnbold (*Zeit. Biol. N.F.*, 1907, 32, 375), by Siegfeld (*Milch. Zent.*, 1907, 3, 288), and by Smedley (*Biochem. J.*, 1912, 6, 451) (*J.S.C.I.*, 1912, 31, 1091), but the matter was approached in a much more thorough manner in 1917 by Crowther and Hynd (*Biochem. J.*, 1917, 11, 139), who used an extended modification of the method of alcoholysis originally used by Haller (*C.R.*, 1906, 143, 657) and later by many other workers for various purposes (see page 51). They endeavoured, and apparently with some success, to make the method quantitative and for the first time a really complete analysis of butter fat was deduced. Their results, together with those of other workers, are given in the following table. The results of Holland and Buckley obtained by a very similar method were published in America in the following year (*J. of Agri. Res.*, 1918, 12, 719).

TABLE CCI.—HOLLAND AND BUCKLEY'S RESULTS

Fatty Acids.	Amount Present.
Soluble acids—	Per cent.
Butyric acid	3·2
Caproic acid	1·4
Caprylic acid	1·0
Capric acid	1·8
Total	7·3
Insoluble acids—	
Lauric acid	6·9
Myristic acid	22·6
Palmitic acid	19·2
Stearic acid	11·4
Oleic acid	27·4
Total	87·5
Soluble and insoluble acids—	
Total	94·8

The percentages, which are the percentages of fatty acids in the fat are, in the original, given to three places of decimals—this is, of course, absurd.

The work of Holland and Buckley has been followed up by Holland and his co-workers and further work has been somewhat recently published (*J. of Agri. Res.*, 1923, 24, 365). These results are summarised in the following tables :

TABLE CCII.—SUMMARY OF HOLLAND'S INVESTIGATIONS OF FATTY ACIDS IN BUTTER FATS

Fatty Acids.	Animal 1.	Animal 2.	Animal 3.	Animal 4.
	Per cent.	Per cent.	Per cent.	Per cent.
Soluble acids—				
Butyric acid (by difference)	2·3	2·9	3·0	2·7
Caproic acid	1·6	1·7	1·8	1·3
Caprylic acid	·6	·7	·9	·8
Capric acid	2·0	1·7	1·5	1·7
Total	6·5	7·0	7·2	6·5
Insoluble acids—				
Lauric acid	7·6	6·3	5·6	6·6
Myristic acid	19·8	17·5	20·5	21·8
Palmitic acid (by difference)	14·8	16·2	12·3	22·9
Stearic acid	12·1	14·9	17·8	11·8
Oleic acid	34·1	32·9	31·3	25·3
Total	88·4	87·8	87·6	88·4
Total fatty acids	94·9	94·8	94·8	94·9

TABLE CCIII.—FATTY ACIDS IN BUTTER FAT FROM COWS EARLY IN LACTATION

Fatty Acids.	Animal 1.	Animal 2.	Animal 3.	Animal 4.
	Per cent.	Per cent.	Per cent.	Per cent.
Soluble acids—				
Butyric acid (by difference)	3·2	..	3·0	4·2
Caproic acid	2·2	..	1·9	2·4
Caprylic acid	·8	..	1·0	·7
Capric acid	1·5	..	1·5	1·3
Total	7·7	8·0	7·4	8·6
Insoluble acids—				
Lauric acid	4·9	4·8	4·5	4·8
Myristic acid	20·1	18·4	19·1	20·7
Palmitic acid (by difference)	13·4	15·8	13·4	14·2
Stearic acid	15·2	16·2	20·4	18·1
Oleic acid	33·5	31·5	30·0	28·3
Total	87·1	86·8	87·4	86·1
Total fatty acids	94·8	94·8	94·8	94·7

TABLE CCIV.—FATTY ACIDS IN BUTTER FAT FROM COWS INTERMEDIATE IN LACTATION

Fatty Acids.	Animal 1.	Animal 2.	Animal 3.	Animal 4.
	Per cent.	Per cent.	Per cent.	Per cent.
Soluble acids—				
Butyric acid (by difference)	2·5	2·8	2·5	3·0
Caproic acid	2·1	2·0	1·9	2·3
Caprylic acid	·8	·7	1·0	·9
Capric acid	1·3	1·2	1·4	1·4
Total	6·7	6·7	6·8	7·6
Insoluble acids—				
Lauric acid	5·4	4·5	5·4	5·3
Myristic acid	19·2	19·6	21·3	20·8
Palmitic acid (by difference)	13·6	13·7	16·2	15·5
Stearic acid	14·9	15·6	18·0	15·9
Oleic acid	35·0	34·7	27·1	29·8
Total	88·1	88·2	88·0	87·2
Total fatty acids	94·8	94·9	94·8	94·8

TABLE CCV.—FATTY ACIDS IN BUTTER FAT FROM COWS LATE IN LACTATION

Fatty Acids.	Animal 1.	Animal 2.	Animal 3.	Animal 4.
	Per cent.	Per cent.	Per cent.	Per cent.
Soluble acids—				
Butyric acid (by difference)	2·2	2·5	2·9	3·1
Caproic acid	1·8	1·8	1·7	2·3
Caprylic acid	·7	·7	·9	·6
Capric acid	1·9	1·6	1·8	1·6
Total	6·5	6·6	7·3	7·5
Insoluble acids—				
Lauric acid	7·7	6·6	7·1	6·3
Myristic acid	15·6	17·1	19·0	18·5
Palmitic acid (by difference)	5·8	9·3	13·1	10·9
Stearic acid	19·1	18·0	18·4	18·8
Oleic acid	40·3	37·4	29·9	32·8
Total	88·5	88·4	87·6	87·3
Total fatty acids	95·0	95·0	94·9	94·8

TABLE CCVI.—FATTY ACIDS IN BUTTER FAT AS AFFECTED BY VARIOUS RATIONS

Fatty Acids.	Varying Ration of Cows: A_2.	A_5.	A_{10}.
	Per cent.	Per cent.	Per cent.
Soluble acids—			
Butyric acid (by difference)	3·4	3·1	3·5
Caproic acid	1·7	1·9	2·1
Caprylic acid	·8	·8	·5
Capric acid	1·6	1·5	1·2
Total	7·6	7·3	7·3
Insoluble acids—			
Lauric acid	5·8	5·4	4·9
Myristic acid	20·7	20·3	20·9
Palmitic acid (by difference)	20·5	22·3	19·1
Stearic acid	9·0	8·7	10·7
Oleic acid	31·2	30·8	31·9
Total	87·2	87·5	87·5
Total fatty acids	94·8	94·8	94·8

Fatty Acids.	Varying Ration of Cows: B_2. Preliminary.	B_4. Coconut Oil.	B_6. Peanut Oil.	B_8. Corn Oil.	B_{10}. Soy-bean Oil.
Soluble acids—					
Butyric acid (by difference)	2·7	2·6	3·1	3·2	2·9
Caproic acid	2·3	2·0	1·9	1·8	1·8
Caprylic acid	·8	·4	·5	·4	·5
Capric acid	2·0	1·5	1·0	1·1	1·0
Total	7·8	6·5	6·6	6·6	6·2
Insoluble acids—					
Lauric acid	6·2	8·0	4·7	4·6	4·8
Myristic acid	22·1	25·0	17·2	16·4	16·1
Palmitic acid (by difference)	20·2	17·1	11·3	9·3	8·7
Stearic acid	7·8	8·6	13·0	13·3	13·4
Oleic acid	30·8	29·5	42·3	45·0	45·8
Total	87·0	88·3	88·4	88·5	88·8
Total fatty acids	94·8	94·8	95·0	95·1	95·0

TABLE CCVII.—FATTY ACIDS IN 21 SAMPLES OF BUTTER

Fatty Acids.	Average.	Range.
	Per cent.	Per cent.
Soluble acids—		
Butyric acid (by difference)	2·9	2·2–4·2
Caproic acid	1·9	1·3–2·4
Caprylic acid	·8	·5–1·0
Capric acid	1·6	1·2–2·0
Total	7·2	6·5–8·6
Insoluble acids—		
Lauric acid	5·8	4·5–7·7
Myristic acid	19·8	15·6–22·6
Palmitic acid (by difference)	15·2	5·8–22·9
Stearic acid	14·9	7·8–20·4
Oleic acid	31·9	25·3–40·3
Total	87·6	86·1–88·5
Total fatty acids	94·8	94·7–95·0

The agreement between the results of Holland and his co-workers and those of Crowther and Hynd is not particularly good, and although the variations recorded may be those which actually occur with different samples of butter fat, yet it is somewhat difficult to reconcile the 2·2 per cent. of butyric acid found by Holland in one case (and determined by difference) with the 4–4·4 per cent. found by Crowther and Hynd. In the present state of our knowledge of this subject the results of Crowther and Hynd have a greater claim to accuracy as the methods adopted, although not above criticism, seem to be somewhat more sound than those of Holland. The subject is in need of further investigation. The stearic acid content of butter fat is dealt with more fully on page 397.

For the decomposition of butter see *Analyst*, 1925, 50, 64, 144.

The amount of phosphorus in butter has been found by Cuisick (*Analyst*, 1921, 46, 50) to be from 0·025–0·041, expressed as P_2O_5. Supplee found from 0·04–0·07 per cent. of lecithin and stated that there are indications that fishy flavour in butter is caused by trimethylene produced from the lecithin. The sterol content is discussed by Kedrovitsch (*Analyst*, 1912, 37, 497); Steuart (*ibid.*, 1923, 48, 155) and by Fox and Gardner (*ibid.*, page 227).

The phytosterol of coconut oil has been examined by many observers, and a large number of results for the M.Pt. of the acetate have been obtained. Juckenach and Pasternack (*Z. f. U. N. und Genuss*, 1906, 11, 156) give the M. Pt. of the phytosteryl acetate of butter from cows fed on coconut cake as 113°. Barthel and Sorden (*Analyst*, 1914, 39, 254) found that the cholesteryl acetate obtained from pure Swedish butters had M.Pt. 114·1°–115·3°, whilst in the case of animals fed on coconut cake it was 115°–115·9°. The addition of 10 per cent. of coconut oil to genuine butters raises the M.Pt. to 116·2°–117·1°. The highest M.Pt. of the cholesteryl acetate of butter fat obtained by Harris (*Analyst*, 1906, 31, 353) was 115·4° (corr.).

TABLE CCVIII.—CONSTANTS OF BUTTER FAT

Authority.	S.G. 100°/15·5°.	M.Pt. °C.	I.V.	Sap. Value.	R.I.	R.M.	Pol.	Kir.	M.Pt. Fatty Acids. °C.	Titre. °C.
Parry . .	·8668–·8705	29–33 (34)	26–28	220–234	1·4533–1·4562	..	..	..	..	..
Leach . .	·867–·870	28–33	26–38	227	1·4531–1·4538	25–34·8	..	..	28–31	..
Richmond	·865–·8685	29·5–33	32–42	218–235	1·4531–1·4567	14–40 (25–34) 28·4 average	1·7–3·2	..	..	..
Fryer and Weston	·936–·942 at 15·5°	28–34	26–38	220–232	1·4542 1·4552	23–30	1·7 2·9	20–26	..	33–37
Mitchell .	..	..	31–50	210–229	1·4524 1·4558	17–33	..	..	38–40	33–35
Revis and Bolton	..	33–45	..	..	..	20–33	1·6–3·5	..	..	..

Specific Gravity.—The determination of the specific gravity of butter fat has not that importance now which it had years ago on account of the practice of other methods of adulteration and the working out of new and more useful methods of anlaysis—nevertheless it may sometimes be of value and should perhaps be carried out in cases of difficulty. The temperature for the determination which has been chosen by various observers has varied from 15·5° to 100°, but as a general rule temperatures below the melting-point have not been extensively used. In the following table the ranges obtained at the various temperatures noted have been collected:

Temperature.	Range of S.G.	Authority.
15·5°/15·5°	0·936–0·942	Fryer and Weston
100° F./100° F.	0·9094–0·9135	Bell, Thorpe, Richmond
40°/40°	Not less than 0·905	U.S. standard butter
100°/15·5°	0·8645–0·8685 *	Allen, Russian Government, Richmond.

The practice of the determination of the specific gravity was first developed at the British Government Laboratory by Bell, who used a temperature of 100° F. (37·8°). This temperature is a suitable one on account of the fact that at about this temperature, as has been shown by Shalweit, the greatest differences are obtained between the specific gravities of butter and oleo margarine. Shalweit's results are given in the following table:

* One or two apparently genuine samples gave results as low as 0·863-0·864.

TABLE CCIX.—SPECIFIC GRAVITIES OF BUTTER, MARGARINE AND LARD AT VARIOUS TEMPERATURES

Temperature. °C.	Butter.	Margarine.	Difference.	Lard.
35	0·9121	0·9017	0·0104	0·9019
50	0·9017	0·8921	0·0096	0·8923
60	0·8948	0·8857	0·0091	0·8859
70	0·8879	0·8793	0·0086	0·8795
80	0·8810	0·8729	0·0081	0·8731
90	0·8741	0·8665	0·0076	0·8668
100	0·8672	0·8601	0·0071	0·8605

A number of observers, however, prefer the temperature of 100°/15·5° so that the figures for this temperature are given although it is not so useful as the lower temperature. In the following table average figures are given for a number of oils and fats likely to be used as butter adulterants at the two temperatures usually used in the case of butter and also at 15·5°/15·5°:

TABLE CCX.—SPECIFIC GRAVITIES OF VARIOUS FATS USED TO ADULTERATE BUTTER

Oil.	S.G. 100°/100° F.	S.G. 100°/15·5°.	S.G. 15·5°/15·5°.
Butter fat	0·912	0·866	0·938
Lard	0·906	0·860	0·936
Tallow	0·903	0·860	0·947
Cotton-seed oil	..	0·872	0·923
Sesamé oil	..	0·867	0·923
Soy-bean oil	..	..	0·925
Arachis oil	..	0·863	0·917
Coconut oil	0·917	0·874	0·926
Palm-kernel oil	..	0·873	0·952

It follows from these figures that it is quite easy to adulterate butter fat in such a way that no indication of the fact would be given by the specific gravity. In spite of this, however, the relationship which this bears to the other constants, notably to the iodine value and saponification value, is not always unimportant and may give useful information. As a rule this is a determination which is not made and as a sorting test it is useless.

The glycerides of the lower fatty acids increase the specific gravity so that in general the specific gravity will vary with the Reichert-Meissl value; this variation is discussed further on, page 393.

The Reichert-Polenske Value.—The Reichert-Polenske value (which for all practical purposes may be taken to have the same value as the Reichert-Wollny number which it supplants) is characteristic of butter, so characteristic in fact that the test was first devised to distinguish pure from adulterated butter and this very fact has led many observers into expecting too much from its indications. Like many other processes it is an excellent slave but a very bad master and this fact should never be lost sight of when its indications come up for judgment.

The test is the one which should always be carried out as a matter of

routine. Where the value exceeds 28 and the Polenske value is within the usual limits (see Polenske value below) the butter may be accepted as genuine, particularly if the refraction figure and the Valenta test are within the usual range, although the possibility of the addition of artificial esters should not be lost sight of. The presence of benzoates or salicylates will also tend to increase the observed value as has been shown by various observers. Where the value falls between 26 and 28 the sample will, as a general rule, prove to be genuine, but the possibility of adulteration is by no means remote and before such samples are reported as genuine one or more corroborative tests should be performed. When the Reichert figure falls below 26 the probability of adulteration increases greatly, although a number of undoubtedly genuine butters have been examined whose Reichert values have been as low as 17—such samples are, however, quite exceptional, but their existence should be sufficient to breed care in the analyst's mind and cause the exercise of due deliberation before any sample is reported as adulterated on the Reichert value alone. The Final Report of the Butter Committee recommended (*inter alia*), with some dissentients, that the figure 24, arrived at by the Reichert-Wollny method, should be the limit below which a presumption should be raised that butter is not genuine, but this figure has never been officially accepted. It has, nevertheless, become a very usual non-official standard in this country, although the adoption of such a figure which will allow the addition of 15 to 20 per cent. of foreign fat to an average butter and 25 to 30 per cent. to a butter with a high Reichert figure has obviously many disadvantages. There is only one point which requires more care than the report of a butter as genuine and that is a report that it is adulterated. Further remarks on this point will be found under interpretation of results on page 392.

A large number of Reichert figures are available in literature on samples of genuine butter from all countries. Many of these were submitted to the Departmental Committee, the *Minutes of Evidence* of which should be consulted for full details. The following table gives in condensed forms much of the evidence on many points which has been made available:

TABLE CCXI.—AVERAGE REICHERT FIGURES ON VARIOUS BUTTER SAMPLES

Observer.	Type of Butter.	No. of Samples.	Range of Figures.	Average.
[1] Brownlee . . .	Irish	127	19·5–30·8	..
Richmond . . .	Various	700	21·2–35	28·4
Allen	,,	..	25–32	28
Hehner	,,	..	22–	29
Dutch Gov. Lab.. .	Dutch	777	21·5–33·4	..
Rifle	Norwegian	650	21·1–34·9	29·7
Thorpe	English	357	22·5–32·6	..
Lewing	Russian	320	24·5–30·5	..
Russian Gov. Lab. .	,,	352	20·4–30·5	25·8
[2] Van Rijn . . .	Dutch	428	17–33	25
Lewkowitsch . . .	Finnish	..	24·0–32·0	27–32
Wauters	Belgian	755	19·8–36·9	26–33
Holm and Kvarup .	Danish	7834	22·4–33·3	..

[1] *Proc. Roy. Dublin Soc.*, 1925, 18, 49.

[2] From individual cows figures varied from 16·8–40·0.

It follows, therefore, from these figures that the larger the herd and the more uniform and usual the condition of life of the animal the more " normal " will be the milk fat.

Many thousands of Reichert determinations have come under the notice of the writer, the average of which has been 28 to 29, with only quite a small proportion below 25–26. It may be assumed that any butter having a Reichert value below 26 is suspicious and should be further examined, whilst even above this figure a sample is not necessarily genuine. Low Reichert values are usually caused (this refers to the butter fat from the mixed milk of a herd, individual cows may easily give " abnormal " butter fats) by exposure of the cows to cold or other adverse conditions, or by the lateness of the lactation period. There is abundant evidence to show that the proportion of the lower fatty acids is appreciably less during the last month or so of lactation.

The following conclusions due to Crowther taken from *Report No.* 66 *of the University of Leeds* and the *Yorkshire Council for Agricultural Education* well summarises our present knowledge.

This states that " the chief factors affecting the proportion of volatile acids present (as fats) in butter fat are :

" (*a*) The stage of lactation of the cows.

" The proportion of volatile acids is highest in the early stages of lactation and tends to decrease greatly towards the end.

" (*b*) Climatic and other conditions that may affect their comfort.

" Conditions tending to produce discomfort of the cows (*e.g.*, trying climatic conditions, draughty or stuffy byres, irregularity in milking, etc.) probably tend in most cases to lower the proportion of volatile acids present in the butter fat. The effects probably vary greatly with the differences in nervous temperament of different cows.

" (*c*) The character of their food.

" The evidence available as to the influence of the food of the cow on the proportion of volatile acids present (as fats) in the butter fat is, in some respects conflicting, but apparently the proportion is highest when the food contains easily fermentable matter, e.g., green food, " roots," sugar, etc. Oil-cakes have less effect on the proportion of volatile acids than on other characteristics of the butter, e.g., colour, texture, flavour, etc. The effect on these latter is, however, so marked that it is, in general, unwise to use very large quantities of such foods for butter production. An allowance of 4 lb. per head per day is suggested as a working maximum.

" No connection has yet been established between the proportion of volatile acids in a sample of butter and its quality as indicated by taste, aroma, texture, etc."

The following figures, taken from page 507 of the *Minutes of Evidence to the Final Report of the Departmental Committee on Butter Regulations* indicate the influence of the lactation period upon the Reichert figure.

	Lactation Period in Months.									
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Whole year .	30·9	29·5	29·1	27·7	26·2	27·5	25·9	24·0	26·2	22·0
Oct.–March .	31·5	31·8	31·0	30·4	25·4	..	23·3	24·0	26·2	22·0
April–Sept. .	29·6	28·8	28·8	27·1	26·9	27·5	28·1	..	..	..

It would appear that the quality of the butter as judged by its market value bears no relationship to the Reichert value. This is shown in the following table, which consists of samples of Danish dairy butter showing the Reichert figure found by analysing the butter fat, and the character of the butter given at the State butter shows (*Minutes of Evidence to the Final Report of the Departmental Committee on Butter Regulations*, pages 493 and 494).

TABLE CCXII.—ANALYSIS OF VARIOUS DANISH BUTTERS

R.	Character.	R.	Character.	R.	Character.
33·0	9·8	25·9	10·4	23·7	5·3
30·1	10·6	25·8	11·4	23·7	10·1
29·6	5·9	25·7	9·0	23·6	8·8
29·3	8·2	25·7	3·8	23·3	4·0
29·1	11·1	25·5	8·0	23·2	10·9
28·7	9·1	25·3	9·0	23·1	9·7
28·5	4·6	25·1	8·9	22·9	9·4
28·3	10·0	25·0	9·0	22·8	9·7
27·4	6·9	25·0	8·4	22·7	6·3
26·8	8·7	24·8	8·2	22·5	8·9
26·3	11·1	24·6	9·1	22·5	6·6
26·2	9·9	24·6	6·9	22·4	8·7
..	..	24·6	8·0	22·3	7·4
..	..	24·5	7·8	22·2	9·4
..	..	24·5	2·9	22·1	9·6
..	..	24·5	8·6	22·1	9·7
..	..	24·1	10·2	21·8	8·2
..	..	24·1	7·3	21·5	8·7
..	..	24·1	10·0	20·0	7·9
Average for each group 28·6	8·8	24·9	8·3	22·5	8·4

This is seen more plainly from the averages of the three columns where the samples are grouped by their chemical composition in three groups, those with Reichert above 26, those with R. between 26 and 24 and those with R. below 24.

	Reichert Figure.	Character of Butter.
R. from 33–26	28·6	8·8
„ „ 26–24	24·9	8·3
„ „ 24–20	22·5	8·4

This table shows that the average character or quality of the butter in each group is so nearly alike that the difference is insignificant, notwithstanding the great difference in the chemical composition of the butter fat in the different groups.

The Polenske Value.—It was originally claimed by Polenske that this figure, obtained by his process, bore a more or less strict relationship to

the R.M. value as set out in the following table compiled by him. The table, however, must not be slavishly followed as it was compiled from a far too small number of samples.

TABLE CCXIII.—REICHERT-MEISSL VALUES, AND POLENSKE VALUES CORRESPONDING TO SAME (BUTTER FAT)

No.	Reichert-Meissl.	Polenske.	No.	Reichert-Meissl.	Polenske.
1	19·9	1·35	18	26·2	1·9
2	21·1	1·4	19	26·5	1·9
3	22·5	1·5	20	26·6	1·8
4	23·3	1·6	21	26·7	2·0
5	23·4	1·5	22	26·8	2·0
6	23·6	1·7	23	26·9	2·1
7	24·5	1·6	24	26·9	1·9
8	24·7	1·7	25	27·5	1·9
9	24·8	1·7	26	27·8	2·2
10	24·8	1·6	27	28·2	2·3
11	25·0	1·8	28	28·4	2·3
12	25·1	1·6	29	28·8	2·2
13	25·2	1·6	30	28·8	2·5
14	25·3	1·8	31	29·4	2·6
15	25·4	1·9	32	29·6	2·8
16	25·6	1·7	33	29·5	2·5
17	25·4	1·7	34	30·1	3·0

Richmond has deduced a formula which gives the relationship between the Polenske and the Reichert value.

$$R \times 0{\cdot}033 - 0{\cdot}62 = \log_{10}(P - 0{\cdot}48)$$

and gives the following table for the maximum permissible Polenske value corresponding to the various Reichert values.

TABLE CCXIV.—MAXIMUM PERMISSIBLE POLENSKE FIGURES CORRESPONDING TO REICHERT VALUES

Reichert Figure.	Polenske Figure.		
	Mean.	Calculated.	Maximum.
32	3·2	3·24	3·7
31	3·0	3·04	3·5
30	2·8	2·85	3·3
29	2·7	2·68	3·2
28	2·6	2·51	3·1
27	2·4	2·37	2·9
26	2·3	2·23	2·8
25	2·1	2·14	2·6
24	2·0	2·02	2·5
23	1·9	1·87	2·4
22	1·8	1·77	2·3
21	1·7	1·70	2·2

When the Polenske figure exceeds the maximum given in the above table for the corresponding Reichert figure coconut oil may be present and its quantity may then be calculated from the formula

$$\% \text{ C.N.O.} = \frac{P - P'}{14{\cdot}4} \times 100.$$

Where P = Polenske figure and P′ is the mean Polenske figure taken from the table corresponding to the R. figure to which has been added half the Polenske figure found. Thus supposing that a butter had R. of 23 and a Polenske or 3·3

$$\% \text{ C.N.O.} \begin{cases} = \frac{3{\cdot}3 - 2{\cdot}0}{14{\cdot}4} \times 100 \\ = 9 \text{ per cent.} \end{cases}$$

Where there are indications that palm-kernel oil is present (for methods of determination see pages 333, etc.) the figure 8·5 should be substituted for 14·4 in the above equation. Other oils such as babassu may, of course, be present (q.v.) and the possibility of their presence should not be overlooked. High Polenske figures are given by the fat of goat's butter, etc., see page 402.

The Polenske value also shows a relationship with the Kirschner value (q.v.). The M.Pt. of the acids obtained in the Polenske process may be useful. (Cf. coconut oil, page 337, and *Analyst*, 1921, 46, 187.)

The Kirschner Value.—Whilst the Kirschner value is of primary importance for the detection and determination of small quantities of butter in margarine (q.v. also coconut oil, page 334) it has been shown by Revis and and Bolton and by Cranfield that the relationship between the Polenske value and the Kirschner value is more sensitive to the addition of coconut oil than that between the Reichert and Polenske values. Thus Bolton, Revis and Richmond (*Analyst*, 1912, 37, 183) state that the presence of coconut oil may be inferred if the Polenske figure is more than 1·0 c.c. higher than that given in the following table for the corresponding Reichert value:

Kirschner Figure.	Polenske Figure.
26	3·2
24	2·6
22	2·1
20	1·6

Cranfield (*ibid.*, 1915, 40, 439) has studied these results and he finds the following corresponding figures:

Kirschner Figure.	Polenske Figure.	
	Average.	Limits.
24–24·4	2·6	2·6–2·7
23–24	2·4	2·2–2·6
22–23	2·4	1·8–2·9
21–22	2·1	1·7–2·7
20–21	1·7	1·4–2·2
19–20	1·5	1·4–1·7

The writer has carried out a large number of analyses and finds that the above relationships hold good in general, but that exceptions do occur.

From Cranfield's results Richmond (*ibid.*, 1919, 44, 166) has calculated the relationship as $P=(K-14)\times 0{\cdot}26$, which gives a maximum error in Cranfield's individual results of 0·7 c.c. Richmond states that the presence of coconut oil or some similar oil may be safely assumed if the Polenske figure is higher than $(K-10)\times 0{\cdot}26$.

Although the above formula will undoubtedly give correct figures in all normal cases yet one must not lose sight of the fact that several observers have obtained abnormally high Polenske figures in cases where the animals had been fed on turnips or beetroot leaves and turnip leaves. Lewkowitsch also has reported Polenske figures as high as 4·1 (with a Reichert figure of 31·4).

Siegfeld's results, which are abnormally high, are given in the following table (*Z. f. Unter. d. N. u. G.*, 1909, 17, 179):

Reichert Value.	Polenske Value.
24·5	2·1
29·1	4·1
30·2	3·3
30·5	3·1
31·6	4·9
33·5	4·4
35·4	5·0
40·3	6·2

The quotation of these figures taken in conjunction with those given above will probably give quite sufficient warning of their relative importance.

Refractive Index.—Before the introduction of coconut oil and similar products the refractive index was a most useful sorting test in so far as it is so easily applied; thus those butters having a refraction figure of less than, say 43·5 at 40° ($n=1{\cdot}4545$) could be classed as genuine without further examination, whilst butters having higher figures were dealt with further. A higher figure than this was used by some observers, thus Wollny suggested 44·2 at 40° as a limit below which no adulterated butter would fall and certainly the majority of adulterated samples would fall outside this limit yet, since a figure of 42 is not altogether unusual for a pure butter, it is obvious that in such a sample a refraction figure of 44·2 (or even 43·5) would cloak a considerable amount of adulteration—with this reservation, therefore, the test was a valuable one.

Seeing that the refraction figure for coconut oil is about 36 ($n=1{\cdot}4495$) and that for animal fats about 50 ($n=1{\cdot}4593$) it is obvious that mixtures of these can be prepared giving refraction figures covering the whole range of those for pure butter and, therefore, as a sorting test, the refraction figure is now worse than useless. The test is, however, still not without value as an additional aid to be taken into consideration with other constants. The average figure for butter at 40° is from 42·5–44 ($n=1{\cdot}4542$ to $1{\cdot}4552$), but much higher and lower figures than these have been recorded as set out in the following table:

TABLE CCXV.—REFRACTION FIGURES FOR VARIOUS BUTTERS

Observer.	Source.	No. of Samples.	Range. B.R. 40°.	n^{40}.
Thorpe . . .	English	357	39·7–45·9	1·4522–1·4565
Stein	Russian	26	42·7–46·2	1·4543–1·4567
Rifle	Norwegian	650	41·4–46·4	1·4534–1·4569
Van Rijn . . .	Dutch	95	43·6–46·7	1·4549–1·4571
„ „ . . .	„	368	41·6–48·0	1·4536–1·4580
Richmond . .	Various	700	41·1–46·3	1·4532–1·4568
Bakst and Lenin .	Russian	352	42·0–46·6	1·4538–1·4570

A few figures have been published which fall outside the above range (e.g., Salomone for five samples of butter from Tripoli and Cyrenia gave 37·5–40·6 at 40°), but as a general rule the range 40–46 will cover all genuine butters.

Saponification Value.—This was, at one time, a most important determination, but is now only used in the case of suspicious samples where the indications obtained may be of value when taken into conjunction with the other values. The usual variations are from 220–232, although, as will be seen from the following table, much wider variations are frequently found; 227 may be taken as the average value.

TABLE CCXVI.—SAPONIFICATION VALUES

Observer.	Source.	Number of Samples.	Range.
Richmond	Various	..	220–230
Stein	Russian	26	217–223
[1] Thorpe	English	347	216–238
Bakst and Lenin . . .	Russian	243	217–229
[2] Siegfeld	Fed on turnips	..	233–243
Van Rijn	Dutch	368	209–230

[1] One sample 214. [2] Cf. *U.N.C.*, 1907, 13, 517.

A high saponification value usually accompanies a high Reichert value and *vice versa*, but this is not always the case, *vide* p. 393 below.

The Iodine Value.—This figure is of value on account of the fact that its indications are to a certain extent independent of the Reichert and Saponification values. It is practically a direct measure of the amounts of oleic glycerides present. This is to some extent affected by the nature of the food, there being distinct evidence that linseed cake and other cakes cause an increase in this figure. This matter is discussed more fully under influence of feeding, page 400, and under interpretation of results, page 392. The following table gives a large range of results by different observers :

TABLE CCXVII.—IODINE VALUES

Observer.	Source.	Number of Samples.	Range.
Richmond	Various	..	31·6–42·0
Stein	Russian	26	32·8–44·8
Bakst and Lenin . .	Russian	..	24·5–47·9
,, ,, . .	Russian	..	30·9–48·5
Van Rijn	Dutch	368	30·6–50·3
Siegfeld.	..	..	22·5–53·3

One figure of 72·37 has been given but this would appear to be a misprint. Cows fed on turnips.

The iodine value varies to a very large extent with the refractive index, and even in those cases where the R.W. figure and the refraction have not gone together the iodine figure will still correspond with the refraction. For viscosity see *Analyst*, 1913, 38, 458; *J.S.C.I.*, 1913, 32, 804; 1923, 42, 793A.

A Scheme for the Analysis of Butter Fat with Corroborative Tests.—25–50 grms. of the sample of butter or other convenient quantity should be placed in a small beaker and allowed to melt at as low a temperature as possible. Where a large number of samples have to be examined it is a convenience to have a water-bath with a flat top, having slightly-raised edges, a small vent hole being fitted at one corner to allow of the escape of steam. The fat is then poured off from the curd and water through an open texture filter-paper supported in the top of a similar beaker—a Whatman 11 cm. No. 4 is quite suitable.

The Reichert-Polenske test should be applied in every case, and where the Reichert value is 26 or more and the Polenske value corresponds to this the butter may be accepted in the present state of our knowledge as genuine, although, as has been pointed out above, there is a possibility of adulterated samples being passed. It is not easy to decide what should be done with samples whose Reichert value lies between 24 and 26, because a large amount of work might very easily be done to no useful purpose as the sample would have to be passed in the end—the action in such cases must depend to a large extent upon the special circumstances of each such sample.

In those cases where the Reichert value is less than 24, even when the Polenske value is correspondingly low, the sample should be looked upon with suspicion and further determinations made. The refractive index, saponification value and iodine value should be made and the frequently-scorned Valenta test (cf. *Analyst*, 1920, 45, 19; 1925, 50, 511; *J.S.C.I.*, 1922, 41, 912A.) should not be neglected, and a determination of the melting-point and mean molecular weight of the insoluble fatty acids. The method of Avé-Lallement (see pages 162 and 165) may give useful evidence and cannot be overlooked, but more work needs to be done on this process before its true value can be definitely settled. The usual colour tests for sesamé and cotton-seed oil may be carried out but, as already explained under the appropriate headings (pages 80–83) either positive or negative results here must be treated with circumspection.

Undoubtedly the most difficult task is the determination of even considerable quantities of lard or tallow, as the composition of these fats is some-

what similar to the insoluble acids of butter fat. As the matter stands at present it will not always be possible to decide when small quantities of either of these fats are present, but the first point to consider is the relationship of the various constants one with another. Richmond, basing his work on that of Thorpe, has published the following table showing the general character of the relationship of the various constants in the case of pure butter fat:

TABLE CCXVIII.—GENERAL RELATIONSHIP OF VARIOUS CONSTANTS FOR PURE BUTTER FAT (RICHMOND)

R.W.	P.	K.	Potash absorbed.	Soluble Fatty Acids.	Insol. Fatty Acids.	Mean Molecular Weight of I.F.A.	Iodine absorbed.	Density. 37·8°/37·8°.	Zeiss Refracto-meter at 40.
22·5	1·7	20·0	219·6	4·3	90·1	266·9	45·1	0·9101	44·8
23·5	1·9	21·0	221·4	4·5	89·7	265·5	43·4	0·9104	44·3
24·5	2·1	21·9	223·2	4·7	89·4	265·0	43·0	0·9108	44·3
25·5	2·2	22·4	223·4	4·8	89·3	264·2	40·7	0·9110	44·1
26·5	2·3	22·9	225·4	4·9	88·9	261·9	39·5	0·9113	43·8
27·5	2·45	23·5	226·8	5·2	88·7	261·7	38·8	0·9114	43·4
28·3	2·65	24·2	228·3	5·4	88·4	260·9	37·2	0·9118	42·9
29·5	2·8	24·8	229·9	5·6	88·3	260·1	35·6	0·9120	42·9
30·5	2·95	25·3	231·4	5·8	87·9	259·6	35·0	0·9123	42·5
31·3	3·1	25·9	232·3	5·7	87·9	258·0	34·0	0·9125	42·5
32·6	3·3	27·1	232·6	6·0	87·7	257·8	32·0	0·9130	42·2

Unfortunately, however, such a table is to a considerable extent idealistic, and the following range for the various constants found in a series of 449 genuine Danish butters having Reichert values of less than 25·0 obtained by Faber shows that a very considerable latitude must be allowed:

TABLE CCXIX.—FABER'S RESULTS

Reichert.	Specific Gravity.	Sap. Value.	Refraction at 40°.	Iodine Absorption.
18·4–19·9	862·8–864·1	215·2–217·9	42·4–43·8	42·5–47·2
20·0–20·9	863·6–864·6	215·4–219·8	43·0–44·1	42·6–49·4
21·0–21·4	863·5–864·7	216·7–222·2	41·0–44·1	42·3–48·3
21·5–21·9	863·6–864·6	215·4–219·5	42·8–44·3	42·5–49·1
22·0–22·4	863·7–864·9	216·6–220·6	42·6–44·4	40·9–47·6
22·5–22·9	863·6–865·2	215·8–220·9	42·3–44·5	42·0–49·7
23·0–23·4	863·7–865·1	216·4–222·5	42·0–44·8	39·6–49·2
23·5–23·9	863·6–865·1	216·2–223·9	42·1–44·6	39·5–49·1
24·0–24·4	863·7–865·3	217·1–224·9	41·3–44·6	38·6–49·8
24·5–24·9	863·1–865·7	217·6–224·7	42·0–44·0	40·2–47·3

In order that this subject may be thoroughly understood a large number of complete analyses of genuine butter fats with Reichert values of less than

24 have been collected in the following table from the results of Thorpe, Faber, Lenin, Bakst, Van Rijn, etc., so that the variations of the various figures in the case of genuine butter samples of low Reichert value can be compared with the numbers actually found in the case of a suspicious butter. The final decision must, of course, depend upon all the factors in the particular case, but this table should be of assistance in enabling the analyst to come to a reasonable decision in cases of difficulty, coupled with the more recent methods detailed below and the Avé-Lallemant value.

TABLE CCXX.—VARIATION OF VALUES NOTED

Reichert.	S.G. 100°/100°F.	Sap. Value.	I.V.	Z.B.R. 40° C.	M.M.W.
23·9	910	222	..	43·9	265
23·9	911	219	..	43·9	265
23·9	865[1]	219	41·7	45·5	..
23·9	911	218	..	43·5	265
23·8	865[1]	222	38·9	44·5	..
23·8	910	221	..	44·7	267
23·8	911	218	44·1	45·7	..
23·8	911	218	44·7	45·9	..
23·8	911	217	43·9	45·9	..
23·8	..	216	45·6	46·1	..
23·7	911	221	43·3	46·6	..
23·7	864[1]	219	41·3	44·7	..
23·7	865[1]	219	40·3	45·0	..
23·7	..	219	41·8	45·4	..
23·7	911	219	43·6	45·7	..
23·7	911	218	44·3	45·7	..
23·7	911	218	46·1	46·3	..
23·7	911	217	45·3	46·0	..
23·7	911	217	46·6	46·3	..
23·6	911	222	36·0	43·9	..
23·6	911	220	..	44·2	264
23·6	911	220	..	44·6	259
23·6	912	220	46·4	47·2	..
23·6	911	219	39·6	44·7	..
23·6	911	219	42·8	45·3	..
23·6	911	219	42·2	45·4	..
23·6	911	218	36·4	44·5	..
23·6	864[1]	218	42·5	45·5	..
23·6	911	218	43·8	45·7	..
23·6	911	218	44·7	46·1	..
23·5	911	225	..	42·9	263
23·5	910	218	..	45·2	267
23·5	911	216	43·6	45·7	..
23·5	911	216	44·4	45·9	..
23·5	911	216	43·8	46·0	..
23·5	911	215	44·6	46·3	..
23·5	911	215	45·0	46·3	..
23·4	911	224	..	43·3	263

[1] At 100°/15° C.

TABLE CCXX.—*continued*

Reichert.	S.G. 100°/100°F.	Sap. Value.	I.V.	Z.B.R. 40° C.	M.M.W.
23·4	911	223	34·4	43·2	..
23·4	910	222	..	44·7	265
23·4	910	221	..	44·0	264
23·4	911	221	38·8	44·3	..
23·4	865[1]	218	44·9	46·0	..
23·4	911	217	42·9	44·7	..
23·4	911	217	45·4	46·2	..
23·4	910	214	47·3	47·5	..
23·3	910	225	..	44·4	265
23·3	911	221	38·0	43·9	..
23·3	911	220	38·7	44·2	..
23·3	912	220	42·4	45·4	..
23·3	912	219	50·3	47·0	..
23·3	911	217	43·9	45·5	..
23·3	911	217	43·3	45·6	..
23·3	911	217	45·0	46·3	..
23·3	911	216	44·5	46·0	..
23·3	911	214	44·7	46·0	..
23·2	911	220	..	44·4	266
23·2	911	219	47·2	47·0	..
23·2	911	217	43·5	45·4	..
23·2	865[1]	217	47·3	46·1	..
23·2	911	217	46·2	46·2	..
23·2	911	216	44·9	46·2	..
23·1	910	221	..	43·5	266
23·1	912	221	38·0	46·2	..
23·1	911	218	42·6	45·5	..
23·1	912	218	42·9	45·7	..
23·1	864[1]	218	42·3	46·0	..
23·1	910	218	44·9	46·4	..
23·1	911	217	43·5	45·6	..
23·1	864[1]	217	43·9	46·3	..
23·1	911	217	45·7	46·5	..
23·1	910	216	45·8	46·5	..
23·1	911	209	44·5	35·0	..
23·0	911	222	..	44·7	266
23·0	910	221	..	44·6	267
23·0	911	218	46·4	46·3	..
23·0	911	217	40·7	46·3	..
23·0	911	217	46·7	47·7	..
23·0	911	216	44·1	46·2	..
22·9	911	220	46·2	46·7	..
22·9	911	219	..	45·9	..
22·9	865[1]	217	45·4	46·0	..
22·9	909	216	..	44·4	260
22·6	911	219	45·5	46·1	..

[1] At 100°/15° C.

TABLE CCXX.—*continued*

Reichert.	S.G. 100°/100°F.	Sap. Value.	I.V.	Z.B.R. 40° C.	M.M.W.
22·6	911	217	43·8	46·0	..
22·6	911	216	45·2	46·6	..
22·6	910	213	45·3	46·2	..
22·5	911	222	44·0	45·9	..
22·5	865[1]	221	32·8	43·2	..
22·5	864[1]	221	44·0	46·1	..
22·5	910	220	..	44·8	266
22·5	911	219	43·2	45·8	..
22·5	911	218	45·0	46·3	..
22·5	911	217	43·9	46·0	..
22·5	911	217	45·5	46·5	..
22·5	911	216	43·9	45·9	..
22·4	910	218	..	44·7	269
22·4	911	215	44·6	46·2	..
22·4	910	215	45·4	46·8	..
22·3	912	218	..	45·5	267
22·3	911	218	47·5	46·5	..
22·3	911	217	46·6	46·2	..
22·3	911	216	45·3	46·2	..
22·3	911	216	47·0	46·2	..
22·3	911	216	45·2	46·4	..
22·3	911	215	48·0	46·1	..
22·3	911	213	44·5	46·2	..
22·2	911	218	41·3	45·1	..
22·2	911	218	45·8	46·4	..
22·2	911	215	41·0	45·0	..
22·1	911	215	47·2	46·7	..
22·0	910	222	..	43·7	266
22·0	910	220	..	43·5	266
22·0	864[1]	217	44·2	46·0	..
22·0	911	215	48·1	45·0	..
21·8	911	218	44·9	46·0	..
21·8	864[1]	217	44·8	46·2	..
21·8	910	215	45·2	45·4	..
21·8	911	214	46·0	46·4	..
21·7	..	219	..	43·7	266
21·6	910	220	..	44·3	268
21·6	911	218	46·3	46·0	..
21·6	911	216	47·3	46·6	..
21·6	911	215	47·3	46·8	..
21·5	911	218	41·9	45·3	..
21·5	911	216	44·5	46·0	..
21·5	911	215	46·5	47·3	..
21·4	910	221	44·6	45·9	..

[1] 100°/15° C.

TABLE CCXX.—*continued*

Reichert.	S.G. 100°/100°F.	Sap. Value.	I.V.	Z.B.R. 40° C.	M.M.W.
21·4	863[1]	217	41·7	45·7	..
21·4	911	217	47·8	47·5	..
21·4	911	216	46·2	46·4	..
21·4	911	215	42·9	45·4	..
21·4	911	213	45·6	46·2	..
21·3	910	219	43·0	45·4	..
21·3	911	213	47·1	47·3	..
21·2	865[1]	215	47·6	45·7	..
21·2	911	214	42·1	45·7	..
21·1	910	218	47·2	47·8	..
21·1	911	217	45·5	45·9	..
21·2	910	215	47·9	47·3	..
21·1	911	214	43·8	46·3	..
21·0	911	220	32·8	43·2	..
21·0	911	216	47·9	46·8	..
21·0	911	211	44·9	46·4	..
20·9	911	212	40·0	46·1	..
20·7	910	217	44·4	46·2	..
20·6	910	220	..	44·1	267
20·4	865[1]	214	47·9	46·6	..
20·3	911	216	48·8	47·7	..
20·3	910	214	49·1	47·7	..
20·0	911	216	47·9	47·5	..
20·0	911	216	49·4	48·2	..
20·0	911	213	44·5	46·3	..
19·9	909	215	..	45·5	267
19·7	911	215	47·5	47·3	..
19·4	910	215	..	46·1	267
19·2	911	213	46·6	46·7	..
19·0	911	212	49·2	..	..
18·5	911	214	48·3	..	..
17·6	910	213	..	47·1	..
17·0	910	212	..	47·1	..

These figures have been condensed for convenience and the results obtained are contained in Table CCXXI, which should be compared with those of Richmond, page 393, and Faber, page 393.

Apart from the Avé-Lallement value, which is discussed on page 162, various methods have been suggested for the determination of animal fats in butter fat. Warburton (Lewkowitsch, *Oils, Fats and Waxes*, 5th edit., Vol. II, p. 858) suggested that a determination of the stearic acid by Hehner and Mitchell's process might be valuable, as butter gives a negligible amount, whilst tallow and lard give upwards of 20 per cent.; he further suggested that the proportion of arachidic and myristic acids might also be valuable

[1] 100°/15° C.

TABLE CCXXI.—SUMMARY OF RESULTS

Reichert.	No. of Samples.	Sap. Value.		I.V.		Z.B.R. 40° C.		M.M.W.
		Aver.	Range.	Aver.	Range.	Aver.	Range.	Aver.
23·9–23·6	30	219	216–222	42·7	36·0–46·6	45·3	43·5–47·2	264
23·5–23·1	43	218	209–225	43·9	34·4–50·3	45·5	42·9–47·5	265
23·0–22·6	14	218	213–222	44·9	40·7–46·7	45·9	44·4–46·7	264
22·5–22·1	24	217	213–222	44·3	32·8–47·6	45·9	43·2–46·8	267
22·0–21·6	13	217	214–222	46·0	44·2–48·1	45·4	43·5–46·8	267
21·5–21·1	17	216	213–219	45·3	41·9–47·9	46·3	45·7–47·8	..
21·0–20·6	6	216	219–222	42·0	32·8–47·9	45·5	43·2–46·8	267
20·5–20·0	6	215	213–216	47·9	44·5–49·1	47·6	46·3–47·7	..
19·9–19·1	4	215	213–215	47·1	46·6–47·5	46·4	45·5–47·3	267
19·0–17·0	4	213	212–214	48·8	48·3–49·2	47·1	..	..

and intimated that he had an investigation on these lines well in hand. As, however, the identical words are used in the sixth edition of this work, much assistance cannot be expected from this source. It is possible that success may be looked for along this line but much yet remains to be done. (Cf. Mitchell, *Analyst*, 1924, 49, 515.)

Methods depending upon the melting-points of the glycerides which are described under " Lard " on pages 365–7, may also prove of value in the examination of butter fat.

Bömer's method depends upon the differences between the M.Pts. of the more insoluble glycerides and of the respective fatty acids separated from these. In the case of pure butter this figure is stated not to exceed 1·0°, whereas that for lard varies between 5·2° and 6·9°. The method of Polenske is based on the difference between the melting-point and the solidifying-point of a fat when taken under standard conditions. It is stated that this difference varies between 12·0° and 15·0° in the case of beef fat and butter fat, whilst lard has a difference value of at least 18·5°. It is further stated that butter should not be considered as adulterated with lard or other fat even when the sample gives a higher value than that recorded for pure butters, if a mixture consisting of 75 parts of the sample and 25 parts of beef fat yields a higher value than 15°, and if at the same time the original butter yields a value below that given by the mixture.

Two more recent methods depending upon the ether solubility of the glycerides have been suggested by Amberger (*J.S.C.I.*, 1916, 35, 1077) and by Seidenberg (*J.S.C.I.*, 1917, 36, 1138; 1918, 37, 633A). The former method depends upon the different solubility in ether of the glycerides of butter fat and of fats containing tristearin or β-palmitodistearin. Thirty-one grms. of the clear melted fat at 40°–50° is placed in a warm 400 c.c. flask, which is then filled with ether, closed with a cork, shaken vigorously, and placed in a water-bath. After one hour it is again shaken, replaced in the water-bath for another hour, and shaken again. If there is no appreciable precipitate the butter fat is stated to contain less than 12 per cent. of tallow or the like. If a precipitate is present, it is collected on a filter, washed with 3–4 c.c. of ether containing 20 per cent. of alcohol and weighed; if the weight amounts to 0·4 grm. or more the butter fat is adulterated with a considerable proportion (15 per cent. or more) of tallow or the like.

The method of Seidenberg depends upon solution of the fat in a mixture of two or more solvents (e.g., alcohol and ether), one of which is more volatile than the other and has a greater solvent action upon the glycerides. Air is aspirated through the solution causing a gradual evaporation and considerable decrease in the temperature, and the glycerides which successively separate are removed. In this way a fractionation of the glycerides in the order of their insolubility is effected, and pure products may be obtained by combining similar fractions and repeating the fractionation as many times as is necessary.

In the second paper Seidenberg gives the following details for carrying out the process: Ten grms. of the sample is dissolved in a 150 c.c. graduated cylinder (27 cm. high and 3·1 cm. diam.) in a mixture of ether 90, and absolute alcohol 10 parts by vol., sufficient of the solvent being added to make the total volume 96 c.c. The cylinder is closed by a rubber stopper through which pass a thermometer and two tubes, one short and the other reaching nearly to the bottom of the cylinder. By raising or lowering the thermometer, the surface of the liquid is brought between the 100 and 102 c.c. marks, and air, previously passed through absolute alcohol, is drawn through the solution at such a rate that it is reduced to about the 60 c.c. mark in not more than 12 or less than 8 mins. The temperature is maintained between 10° and 15° by means of a bath of warm water. The volume of the solution is noted at the point where a distinct turbidity appears, the aspiration is stopped, the solution filtered rapidly, and the precipitated glycerides weighed. With pure butter fat the turbidity is produced when the volume is between 44 and 68 c.c. (of 100 samples examined 94 gave a turbidity at a volume between 50 and 60 c.c.). The maximum insoluble residue found with pure butter fat was 0·449 grm. If the volume of the solution at the turbidity-point is more than 68 c.c., the presence of tallow, lard, or hydrogenated fat is indicated; when the volume is lower than 44 c.c., coconut stearine is probably present.

The great disadvantages of these processes is the large amount of solvent which is necessary and also the differences in results likely to be caused by small differences in manipulation. It seems fairly obvious that future progress in the examination of oils depends at any rate to some extent on our ability to isolate the characteristic glycerides from fats and this process of Seidenberg must have careful consideration in this connection. Some experiments have been commenced by the writer, but these have been unfortunately held up for the time being but it is hoped to continue them at some future date. As in all other methods the chief difficulty will be the large variations in the figures obtained from different samples of pure butter, and subsequent work may show that the method is little, if at all, superior to the Valenta test. For the separation of butter fat by diffusion see Hackett and Crowley (*J.S.C.I.*, 1925, 44, B112); for the viscosity of butter fat see White and Twining (*J.S.C.I.*, 1913, 32, 804). The Valenta test should, on no account be overlooked in any case of difficulty as the results obtained are frequently of considerable value. The method adopted is fully described on page 90. When it is carried out in this way the figures for pure butter usually lie round about 37° and the addition of lard or beef fat will materially increase this figure (cf., especially, *Analyst*, 1925, 50, 511). A further test which may also be of value is that of the melting-point of the insoluble acids which usually lies between 38° and 45° and also the mean molecular weight of the insoluble acids. None of these tests will, however, be used as routine methods but they may be of importance in cases of special difficulty where a full report on a particular sample is necessary.

It must be emphasised that much more work remains to be done on these processes before the indications obtained from them can be accepted without reserve.

Where vegetable oils are suspected important confirmatory evidence may be obtained from the phytosteryl acetate test, which may be carried out as given on pages 124, etc. The M.Pt. of the cholesterol isolated from butter fat rarely exceeds 114° even after a large number of crystallisations. Where the vegetable oil present is coconut oil the microscopic test of Hinks, page 331, is valuable and will assist in the identification of small amounts of this oil (cf. Kerr's method, page 360). Appropriate colour tests for cotton-seed and sesamé oils may be employed keeping in mind the limitations of these tests which are discussed under the appropriate headings.

In some cases a definite answer cannot be given. Even apparently straightforward cases are not always easy and the only general suggestion that can be given is to multiply experience and to be cautious in giving opinions.

The Influence of the Food of the Animals on the Composition of Butter.— The fairly constant values which are obtained for average samples of butter must be considered to be due, to a certain extent at any rate, to the more or less uniform diet which cows receive, as variations in the food supplied undoubtedly cause marked differences in the composition of the butter fat.

Siegfeld (*Analyst*, 1907, 32, 256) found that coconut cake given up to 4 lb. per head per day increased the Polenske value from 2·5 to 3·8, whilst the Reichert value was not appreciably changed. A much greater influence was obtained in the case of beetroot leaves and tops, the Reichert value rising in some cases to over 35, the Polenske also increasing in one case to 5·4; at the same time the iodine value dropped from 35 to an average of 28, the minimum figure being 23·8. Similar influences were observed by Nockmann (*J.S.C.I.*, 1911, 30, 974).

Cranfield (*Analyst*, 1911, 36, 445) studied the effect of feeding with coconut cake and linseed cake; he arrived at the following conclusions :

1. It is apparent from these results that feeding has a great influence on the composition of butter fat.

2. The feeding of coconut cake to dairy cows produced a butter which gave a refractometer figure below the normal, while the Polenske number was very high. The Reichert-Meissl number was, however, quite normal.

3. Feeding with linseed cake influenced the butter in respect of the Polenske number, butters from this source giving a figure much below the normal. The refractometer figure was also influenced, a distinct rise being noticeable.

4. Coconut cake produced a butter of good quality, possessing better keeping qualities than butter from linseed or cotton cakes.

Cranfield and Taylor (*Analyst*, 1916, 41, 240) have studied the effect of feeding with dried yeast and decorticated cotton meal and they conclude from their experiments that dried yeast is an excellent food for dairy cows; apart from a slight increase in the Polenske value it had little effect on the composition. Cranfield (*ibid.*, 1916, 41, 336) compared the effect of decorticated ground-nut cake and decorticated cotton cake and found that there was little difference in the composition of the two series of butters, although that produced from the ground-nut cake was somewhat softer owing to some increase in the unsaturated acids. Both were excellent foodstuffs.

Eckles and Palmer (*Analyst*, 1917, 42, 389) found that cotton-seed products lowered the Reichert value and the saponification value and raised

the iodine value and the melting-point—a rather unusual combination since an increase in the iodine value usually accompanies a *decrease* in the melting-point.

Crowther and Woodhouse (*Analyst*, 1918, 43, 62) using 2 lb. of palm-kernel cake per day found slight increases in the saponification value, Reichert and Polenske values, and a fall in the iodine value and the refractive index, but the figures were not very conclusive.

Bengtsson (*Analyst*, 1923, 48, 225) found that babassu cake caused an increase in the Polenske value, a slight increase in the iodine value and a decrease in the melting-point.

From these and other results it is shown that where the animals are fed with any quantity of a particular oil-cake the composition of the milk fat tends to become similar to that of the oil which is being fed. For all ordinary amounts of cake this effect is not very serious and any likely increase in the Polenske value is not likely to lead to wrong conclusions if the remarks on page 390 are kept in mind.

Ghee

Ghee is defined by the Bombay Adulteration of Ghee Act as a substance made exclusively from butter fat, from which the water has been evaporated by heat and which contains no admixture of any substance not derived from the milk of the cow, buffalo, goat or sheep. The butter is usually allowed to become somewhat rancid and is then clarified by melting and decantation. The product is very largely used by the natives in India—a similar product is known in Egypt as samna.

Ghee has, of course, very similar characteristics to butter fat, but on account of the fact that buffalo milk is largely used the Reichert values obtained are frequently considerably higher than those of the latter. Unfortunately the term " ghee " or " ghee butter " has been given in some text-books, particularly on the Continent, to a purely vegetable butter obtained from *Bassia butyracea*. It is pointed out by Bolton and Revis (*vide infra*) that such a term is objectionable and that it has probably arisen through adulteration of the genuine article with vegetable substitutes, such as *B. butyracea;* the term ghee should be confined to clarified butter fat.

We are indebted for our knowledge of the composition of ghee to various workers among whom may be mentioned Bolton and Revis (*Analyst*, 1910, 35, 343; 1911, 36, 392), K. H. Vakil (*J.S.C.I.*, 1915, 34, 320), S. H. Trimen (*Analyst*, 1913, 38, 247), T. K. Ghose (*ibid.*, 1920, 45, 444). The results obtained by these workers appear to arrange themselves in two classes, those with Reichert values above 30 and others with Reichert values below 30. Bolton and Revis (*loc. cit.*), H. D. Richmond (*Analyst*, 1910, 35, 346), C. A. Mitchell (*ibid.*, 1917, 42, 140), T. K. Ghose (*ibid.*, 1920, 45, 444) are strongly of opinion that the Reichert value of ghee is at least 30, whilst other observers claim that in some cases the figure may fall as low as 20. One point, however, must be borne in mind and that is that buffalo ghee will give as a rule higher figures than cow's ghee; the former is far more common. The note by Mitchell is of sufficient importance to reproduce here :

> " There appear to have been several attempts recently to show that pure ghee may have very low Reichert-Meissl values. This may be true in the case of samples made in the laboratory from the milk of single animals, but this in no way proves that such values are to be considered normal, just as has been the case with similar values for butter fat. To admit the validity of such values as a guide to the possible results

obtained from commercial samples is to leave a very extensive loophole to wholesale adulteration. The figures given by Bolton and Revis have been confirmed by Trimen (*Analyst*, 1913, 38, 246)."

Ghose in an examination of 67 samples of buffalo ghee obtained from single animals found the Reichert value to vary from 30·0 to 42·0, whilst 166 samples obtained from the mixed milk of several animals, obtained from various parts of India, gave figures of 29·0 to 39·0; the average of all the figures was 34·5. Ghose states that at a conference of Calcutta chemists in October 1918 a limit of 30·0 was suggested, but that this was afterwards reduced to 28·0 in consideration of the possibility of accidental admixture with cow's ghee.

The following characteristics have been observed by those whose names are attached:

TABLE CCXXII.—CHARACTERISTICS OF GHEE

	Reichert.	Polenske.	Sap. Value.	Iodine Value.	n^{40}.	Avé-Lallement.	Aci Valu
Bolton and Revis	[1] 28·4–	1·4–	224·9–	28·1–	1·4533–	−16·1 to	3·8
	31·5	2·4	229·1	30·8	1·4537	−2·7	7·3
[2] A. K. Menon .	[3] 25·7	..	218·3	..	1·4528	..	1·5
	[4] 18·2	..	206·8	..	1·4556	..	2·0
K. H. Vakil . .	20·5–	..	218·0–	..	1·4548–	..	1·5
	25·3		232·2		1·4558		3·6
S. H. Trimen .	[5] 31·6–	1·4–	228·1–	..	1·4535–	−20 to	..
	36·6	2·3	236·3		1·4539	−4·3	
	[6] 24·4–	4·1–	227·3–	..	1·4540–	−14·2 to	..
	31·2	[7]6·4	235·5		1·4544	−1·3	
[8] Browning and	18·9–	..	..	..	..	..	0·5
Parthasarathy .	30·2						0·8
Ghose	29·0–	..	226·0–	..	1·4524–	..	..
	42·0		[9] 240·0		1·4538		
Hogen and	24·5–	1·0–	218·0–	23·0–	1·4527–	..	..
Griffiths-Jones .	37·0	2·8	235·0	39·7	1·4551		
Trimen (goat) .	20·8 and	6·5 and	224·5 and	..	1·4528 and	+17·6and	..
	22·9	4·9	231·6		1·4549	+0·1	
Trimen (sheep) .	22·9 and	2·8 and	216·6 and	..	1·4552	+9·7 and	..
	26·5	3·1	223·2			+7·7	

[1] Lower figures are given by these authors but they classify the samples as of doubtful purity. [2] *J.S.C.I.*, 1910, 29, 1428. Single samples of doubtful purity? [3] Cow. [4] Buffalo. [5] Egyptian samna. [6] Syrian samna. [7] These high figures are suggestive of goat butter, but the Avé-Lallement figures do not agree; sheep's milk is supposed to be the source. [8] *J.S.C.I.*, 1917, 36, 118, see note by Mitchell above. [9] Not usually above 235.

Bolton has suggested that the low Reichert values may be explained by the overheating of the fat during its preparation. It is possible, however, that some of the high Reichert values are due to rancidity. In the present state of our knowledge it must be assumed that any sample of ghee which has a lower Reichert value than 30 (or 28) must be considered as suspicious, particularly if it is pretended that it has been prepared from buffalo milk; the possible presence of goat's or sheep's milk should not, however, be overlooked.

Bolton and Revis speak very highly of the Avé-Lallement process, but Trimen does not agree entirely with them. Apart from the fact that Trimen has found a sample of butter which gave a positive value the fat of goat's and sheep's milk also give positive values. There is the further point that in some cases it would be possible to add a considerable proportion of adulterant before a positive value was obtained.

Ghee is widely adulterated. Usual or possible adulterants are animal fats, vegetable fats and vegetable oils. The vegetable oils are now largely used for this purpose particularly Bassia fat and similar products. Barnes and Singh (*Analyst*, 1916, 41, 72) have described Poli oil (page 181) as a likely adulterant.

CHAPTER XXVI

MARGARINE

MARGARINE was defined by Section 3 of the Margarine Act, 1887, as " all substances whether compounds or otherwise, prepared in imitation of butter, and whether mixed with butter or not," whilst this was amended by Section 13 of the Butter and Margarine Act, 1907, to " any article of food, whether mixed with butter or not, which resembles butter and is not milk-blended butter." The first butter substitute was made in Paris in 1870 during the Franco-German War owing to the enormously high price of butter. It was produced as the result of experiments made by a Frenchman, Mégé-Mouries, induced by a prize offered by the French Government. The first inventor and several of those following endeavoured to obtain the true butter flavour by artificial digestion of the beef fat with the content of pig's or sheep's stomachs in the presence of sodium carbonate. Later the same result was attempted by churning with milk and a suspension of macerated cow's udder (cf. English Patent 2157 of 1869). Artificial digestion is no longer resorted to, an equally good, in fact a much improved, flavour being produced by treating the milk with suitable cultures of lactic acid bacilli before incorporation into the fats.

More recent innovations (it is open to question whether they may be looked upon as improvements) are the introduction of hydrogenated oils and the use of artificial milk prepared from vegetable sources such as the soya bean (cf. page 194).

The popular prejudice which existed for so long against the use of margarine was doubtless due to the carelessness which existed at one time in its manufacture, and the unpalatable flavour of the resulting product. All this is now happily a thing of the past. To ensure success the manufacture of margarine has to be carried out under conditions of the most scrupulous cleanliness, and the fats used must be fresh and free from all unpleasant flavour, the result being that the final product of all reliable firms is both wholesome and nutritious.

In regard to the earlier ideas on the nutritional value of margarine the following remarks extracted from a publication of the Local Government Board (now the Ministry of Health) will be of interest : " From time to time investigations have been undertaken with a view to ascertaining the comparative nutritive values of margarine and butter. The general conclusion which has been arrived at is that there is no appreciable difference between the nutritive values of these fatty foods. Other experiments have shown that margarine, butter, lard and coconut oil are equally well absorbed. The usual amount of these fatty matters absorbed is from 95 to 98 per cent. of that ingested. It is true that more vegetable oils and fats are being used nowadays than formerly in the manufacture of margarine, but there is no evidence to show that these are less nutritious than animal fats. All the evidence available tends to show that there is little or no difference in this respect between fats and oils obtained from animal or vegetable sources. All fats used for margarine making, whether they are of animal or vegetable origin, must be practically odourless and tasteless : this implies a high degree of refinement and purity. The advantage which butter possesses

over margarine is æsthetic rather than dietetic, and the difference in price between these two represents what the consumer is willing to pay for luxury." These words were written just before the importance of the presence of the vitamines or accessory food substances had been recognised and therefore need to be revised in accordance with more modern knowledge. The subject is more fully discussed on page 469.

To-day margarines are not usually prepared wholly from oils of any one class, but in every case suitable mixtures—sometimes quite complicated ones—are prepared so that a melting-point suitable to the time of year may be obtained. Two main classes may be roughly distinguished, those which contain a large amount of animal oils (the better and usually the more expensive class) and those which consist mostly of vegetable oils (chiefly coconut and cotton-seed oils) and little or no animal oils. Typical examples of formulæ for the fats of these two classes are those which were officially proposed in May 1918 in this country during the European War.

TABLE CCXXIII.—FORMULÆ FOR TYPICAL OLEO AND VEGETABLE MARGARINES

OLEO MARGARINE.		VEGETABLE MARGARINE.	
Neutral lard	15	*Première jus*	15
Première jus	10	Coconut oil	15
Oleo oil	30	Palm-kernel oil	50
Coconut oil	20	Arachis oil	10
Cotton-seed oil	25	Cotton-seed oil	10

The composition of members of each class may differ more or less widely. The writer is very much indebted to Dr W. Clayton for permission to make use of the following formulæ which are taken from his book, *Margarine*, published by Messrs Longmans, Green & Co. This book, which gives a detailed account of the history and modern preparation of margarine should be consulted for further information on these subjects than can be given here. The following formulæ have been found to give satisfactory oleo margarine:

TABLE CCXXIV.—COMPOSITION OF THE FAT OF OLEO MARGARINES

	1.	2.	3.
Neutral lard	29	20	16
Oleo oil	60	55	50
Première jus	..	..	6
Cotton-seed oil	11	14	15
Coconut oil	..	11	13
	100	100	100

Whilst those below are typical of those used in the production of vegetable margarines.

TABLE CCXXV.—COMPOSITION OF THE FAT OF VEGETABLE MARGARINES

	1.	2.	3.
Coconut oil	85	60	45
Palm-kernel oil	..	30	20
Cotton-seed oil	15	10	20
Oleo stearine	..	..	15
	100	100	100

Many Continental countries (e.g., Belgium, Austria, Germany) insist upon the incorporation of 5–10 per cent. of sesamé oil in order to assist in the subsequent detection of the margarine, whilst others use other substances such as potato starch. It has, however, been well pointed out by Lewkowitsch that " the adulterator in defiance of the law, can easily prepare margarine to which no sesamé oil has been added. But even if, by careful supervision, a margarine maker could be prevented from omitting the sesamé oil, it is easy to circumvent the Baudouin test by employing colouring matters, which give a similar reaction to sesamé oil with hydrochloric acid alone. Fendler, as also Lewkowitsch (before a Parliamentary Committee), have shown that if it be attempted to wash out such colouring matters by treating the fat with hydrochloric acid, the treatment must be repeated so often that finally the fat no longer gives the Baudouin reaction, whether sesamé oil be present or not. As the addition of colouring matters is not forbidden, it is obvious that the enforced addition of sesamé oil to margarine cannot be of any lasting help to the analyst. On the other hand, genuine butters have occurred which faintly gave the Baudouin colour test. On the strength of this test these butters would have been judged to have been adulterated with margarine. The colour reaction in these butters is due to part of the chromogenetic substances of sesamé oil having passed into the milk fat of cows fed with sesamé cake. Although very many feeding experiments with sesamé cake have been carried out by a considerable number of observers, no concordant conclusions have been obtained. Whilst Baumert and Falcke, Thorpe, and others have shown that the chromogenetic substance of sesamé oil does not pass into the milk, there are a number of other observers (Vieth, Siegfeld, a.o.) who deny this statement, and state that they distinctly obtained the sesamé oil reaction with butter made from the milk of cows that had been fed on sesamé cake."

Margarines for industrial use by bakers and confectioners, etc., differ somewhat in composition from those intended for household or table use. The following formulæ, for example, may be taken as typical for the manufacture of cake margarine for which a fairly low melting-point (22°–25°) is required:

TABLE CCXXVI.—COMPOSITION OF FAT OF CAKE MARGARINES

	1.	2.	3.
Oleostearine . . .	23	..	..
Première jus . . .	30	..	37
Oleo oil	..	..	21
Coconut oil . . .	..	70	..
Palm-kernel oil . .	..	10	..
Cotton-seed oil . .	47	20	42
	100	100	100

Pastry margarine has usually a considerably higher melting-point (35°–40°) than that of cake margarine (22°–25°) and, of late years, has contained in some cases large amounts of hydrogenated oils. The following formulæ may be taken as representative of the fat of this class of margarine:

TABLE CCXXVII.—COMPOSITION OF FAT OF PASTRY MARGARINE

	1.	2.	3.
Oleostearine . . .	65	50	35
Première jus . . .	15	30	20
Palm-kernel oil . .	..	..	35
Cotton-seed oil . .	20	20	10
	100	100	100

The modern methods of manufacture differ among themselves to a considerable extent both in the actual methods used and in the necessary plant. The method outlined below is in use in one of the newest English factories and gives excellent results. Details of other methods are given in Clayton's *Margarine*.

The respective quantities of the various oils and fats are melted and run into a tank, whilst the requisite skimmed milk prepared in a manner to be described later is placed in a smaller tank alongside. The oil and milk are then run down separate pipes into an emulsifier which consists of cylindrical steam-heated vessels containing mechanically-driven paddles. In these vessels the fats and the milk are thoroughly incorporated and a perfect emulsion is obtained. When the emulsification is completed the mixture is run into cold horizontal drums which also contain mechanically-driven paddles. The mixing process is then continued until the margarine has become solid. It is then delivered by means of an Archimedean screw on to tables where it is immediately packed into boxes and sent into cold stores.

The milk which is used in the process is soured artificially by means of pure cultures of the lactic acid bacillus. It is contained in large vats which are fitted with steam-pipes by which the milk is heated to the desired temperature. The milk which has been treated with the pure culture is then intimately mixed and the whole allowed to stand until the souring process is completed.

The chief points that have to be carefully attended to in order that the best results may be obtained are absolute cleanliness and perfection of emulsion. The need of absolute cleanliness must be emphasised as without it there is no possibility of preparing a margarine of good flavour which will keep well. Machinery is completely dismantled every week and thoroughly cleansed and sterilised. The great importance of this is shown by the fact that some years ago an English margarine factory suddenly developed trouble—many complaints being received of the poor keeping properties of the margarine. The plant was immediately dismantled and thoroughly cleansed and sterilised but the trouble did not abate. Eventually it was discovered that one pipe, only a few inches in length, had been entirely overlooked in some mysterious way and that it had not been cleaned for several weeks—when this point had been corrected no more trouble was met. The cause of rapid development of excessive rancidity in a margarine should be looked for along similar lines. The fact that the emulsion must be as perfect as possible will be fairly obvious, as otherwise it would be impossible to obtain a product of good texture. The important point to watch is to make sure that, the nearly perfect emulsion having been made, the margarine is cooled rapidly before it has time to break. (For further details see Clayton, *J.S.C.I.*, 1919, 38, 113T and *British Association, 2nd Report on Colloid Chemistry*, 1921, page 112.)

In those cases where the process outlined on page 407 is not used—that is to say when the cooled margarine is obtained in the form of flakes or powder—it is worked on tables or in drums to give it the desired texture and appearance, and with the object of incorporating salt, preservatives, colouring matter and sometimes flavouring. At this point, too, certain margarines have had small quantities of butter worked into them so that the product might be sold—however unfairly and unlawfully—as "Margarine blended with Butter." It will be obvious, however, that the mixture under these conditions cannot be as intimate and uniform as in those cases where the butter is mixed with the oils in the liquid conditions.

Colouring Matter.—Although palm oil or maize oil is sometimes used to produce colour in margarine in imitation of butter colour the method usually adopted is to use an artificial colour. At one time annatto and other natural colouring matters were largely used but these have now mostly given place to some kind of oil-soluble coal-tar dye. "Butter colours" are frequently sold containing the colour dissolved in a suitable oil. The quantity of coal-tar colour required is in the region of 2 parts per million.

Preservatives.—By far the most common preservative is boric acid or borax, or a mixture of the two—in fact in recent years other preservatives are seldom found. Many other substances, however, have been used from time to time, the chief being as follows: Salicylic and benzoic acids, fluorides, sulphites, formalin, nitrates, β-Naphthol, etc. The Departmental Committee on preservatives recommended a maximum of 0·5 per cent. of boron preservative expressed as boric acid, but this is most certainly a maximum figure, 0·3 per cent. being the usual. The following figures give the percentage of boric acid for samples bought under the Food and Drugs Acts in Salford during recent years; the new regulations concerning preservatives will doubtless result in almost the complete elimination of all such substances from margarine.

TABLE CCXXVIII.—PERCENTAGE OF BORIC ACID IN SAMPLES OF MARGARINE

Year.	Total Number of Samples.	Per cent. Boric Acid.					
		0·5-0·41.	0·4-0·31.	0·3-0·21.	0·2-0·11.	0·1-0·01.	0.
1914 . . .	8	..	3	1	3	1	..
1915 . . .	21	1	3	8	8	1	..
1916 . . .	61	..	..	27	27	7	..
1917 . . .	106	..	3	50	46	7	..
1918 . . .	11	..	4	3	3	1	..
1919 . . .	22	..	1	4	7	8	2
1920 . . .	23	2	1	5	6	9	..
1921 . . .	20	..	..	5	8	7	..
1922 . . .	20	..	1	14	4	..	1

According to Escales and Schlesinger (*Analyst*, 1922, 47, 171) a so-called "ester margarine" was prepared in Germany by churning "ester oil" (ethyl and glycol esters of fatty acids) with refined oil and milk. A new edible product was also prepared by esterifying stearic acid with isopropyl

alcohol. The resulting ester melts at 24°, has a pleasant taste and can be used as a main constituent of margarine.

Ethyl butyrate and other esters of volatile acids have also been used ostensibly to produce a butter flavour, but the fact that such an addition would give a considerable Reichert value is quite possibly another reason for its use. (*Analyst*, 1909, 34, 50.) The use of such preservatives as benzoic acid (*Analyst*, 1907, 32, 218; 1908, 33, 397; 1913, 38, 68) will also increase the observed Reichert value, but these difficulties are easily overcome, the first by removing the added ester with alcohol (the constants of the fat, especially if containing coconut oil, may be somewhat modified by this treatment) and the second by washing the fat with water or with very dilute sodium carbonate solution.

General articles on the manufacture of margarine are given by Clayton (*J.S.C.I.*, 1917, 36, 1205) and by Watson (Abstract, *J.S.C.I.*, 1921, 40, 159A). The use of hydrogenated fish oil is discussed by Klimont and Mayer (*J.S.C.I.*, 1915, 34, 148). According to Clayton this is never used in margarine in this country, although the author has seen a sample of hard fat in a works in this country which the manager said was hydrogenated fish oil and which was presumably being used in the manufacture of margarine. One objection to the use of hydrogenated fish oils is the possibility that the odour might return after the fat has been kept and become slightly rancid. Other suggestions which have been made are that the quantities of nickel likely to be present are a potential source of danger to health and that the high melting-points of the resulting fats will lead to greater difficulty of digestion. Other workers have shown that the latter fears are groundless. In many cases the nickel is completely removed and even where it is not the amount remaining is quite minute and has been shown by Lehmann (*J.S.C.I.*, 1914, 33, 763) and Bordas (*J.S.C.I.*, 1919, 38, 787A) to be quite harmless. The melting-point of a completely hydrogenated fat is, of course, high and in many cases considerably above blood-heat but, as a matter of fact, such products cannot be used by themselves in margarine manufacture. Frequently the process of hydrogenation is only carried to an extent that will give the required melting-point, but in the case of a harder product it is mixed with liquid oils so that the desired texture may be obtained. Hydrogenation may be deleterious in that the whole of the vitamines may be destroyed during the process. (Cf. page 469.)

The use of oils having toxic properties in margarine is not unknown, whilst harmful results may arise from other sources such as the use of unsuitable flavouring essences. Hertkorn (*Analyst*, 1911, 36, 65) has shown that in some cases the use of amyl esters of fatty acids and also the esters of the lower members of the oleic series may lead to harmful results as such esters are produced by the interaction of potassium cyanide with alkyl halides, ketones, etc., and are usually more or less poisonous. Most of the cases of poisonous margarine have, however, been produced by the use of oils having toxic properties. During the year 1910 a considerable number of cases occurred in Germany of poisoning with the so-called " Backa-margarine." Certain of the flavouring agents were at first suspected (cf. Hertkorn above) but the source of the trouble was finally traced to the use of Cardamom or Maratti fat (Thoms and Muller, *Analyst*, 1911, 36, 542; Reinsch, who called it " Marotty oil," *J.S.C.I.*, 1911, 30, 139). This oil, which had been imported from India by way of Bombay, was a greenish-grey solid substance of the consistency of coconut fat, with an aromatic odour recalling that of bananas. In the purified state it was white to yellowish-white and had only a very faint odour. The following characters have been observed :

TABLE CCXXIX.—CHARACTERISTICS OF CARDAMOM FAT

Observer.	No. of Samples.	R.I. 40.	Acid Value.	Sap. Value.	R.M.	I.V.	Titre. °C.	M.Pt.
Reinsch Crude .	5	1·4725–1·4731	18·8–28·7	203·1–205·3	0·8–1·3	93·0–94·7	58·8–64·5	..
Reinsch Purified .	2	1·4721–1·4730	0·8–7·9	203·5–208·1	0·6–1·1	88·5–94·0	54·0–58·0	..
Thoms & Muller .	..	..	..	201–212	..	88–94·8	54·0–58·0	22–24
German Customs.	..	1·4731	..	202·7	..	97·6	79·1	22–25

J.S.C.I., 1911, 30, 293.

The oil is obviously similar in character to chaulmoogra oil, and Thoms and Muller investigated the source, which they stated to be a species of *Hydnocarpus*, probably *H. kurzii*, Warburg (syn. *Taraktogenos kurzii*, King)—they found it to contain palmitic, hydnocarpic and chaulmoogric acids. They further found that a dose of 0·04 grm. of the oil killed a white mouse within an hour and a half. Lendrick, Koch and Schwarz, however, although, of course, they agree that it is obtained from the *Hydnocarpus* species, do not consider that the oil is obtained from *H. kurzii*. These authors found chaulmoogric and hydnocarpic acids but not palmitic acid. They consider the absence of palmitic acid to be noteworthy, as Power and Barrowcliff (*J.S.C.I.*, 1905, 24, 741) found this acid to be present in *H. kurzii* and *H. anthelmintica* fats, but not in *H. wightiana* fat. They state also that the external appearance of the seeds of *H. wightiana* and *H. venerata* closely resembles that of Ceylon cardamoms (*J.S.C.I.*, 1911, 30, 293). When administered to dogs the fat produced irritation of the mucous membrane of the stomach and caused vomiting; in many cases the symptoms were of a grave nature and were accompanied by convulsions. A complete bibliography is given by Grimme (*J.S.C.I.*, 1911, 30, 918).

Composition of Margarine.—The composition of the non-fatty portion of margarine is, with the exception of the preservative other than salt, very similar in kind to that of butter but considerably less in amount, the amount of curd, for instance, will not, as a general rule, exceed 1 per cent. A complete analysis is not usually necessary, the determination of water and preservative giving the desired information. The direct determination of fat is sometimes required as there are many advantages in fixing a fat standard for margarine in place of a water standard as is usually done. Margarine should certainly contain not less than 80 per cent. of fat.

Methods of Analysis.—Non-Fatty Portion.—The determination of the various non-fatty ingredients such as curd, salt, water and preservative may be carried out in the same way as for butter, pages 427 to 434. As already mentioned the most usual preservative is some compound of boron, the quantity being returned as boric acid.

The Examination of Margarine Fat.—The chemist who has had only a small experience of fat analysis, must be warned that although at times the problem of margarine analysis may be comparatively simple, yet, owing to the increasing number of oils that are being placed on the market suitable for margarine manufacture, the matter is becoming more and more complex,

and frequently it is only possible to state the particular class of oil which has been used, leaving the actual member of the class more or less unidentified. The difficulties are further increased by the somewhat wide variation in the composition of natural products; thus although two different oils may have quite distinct analytical figures if they are of average composition, yet, slightly abnormal oils may approach each other in composition to such an extent as to make identification difficult if not impossible. For the determination of the approximate composition of a mixture of oils and fats it is necessary, therefore, to assume that each constituent has an average composition. As a general rule this is a legitimate assumption and one which does not lead to serious error. From the above remarks it will be seen that it is not infrequently impossible to detect admixture with oils where the amount of any one of the ingredients falls much below 10 per cent., except where a colour test is available or where, as in such cases as butter or arachis oil, some characteristic and easily determined glycerides are present. This fact is not, however, of very great importance; it merely suggests caution in the interpretation of analytical results, especially in the hands of the inexperienced. (Elsdon, *Chemical Age*, 1923, 8, 450.)

Preparation of the Fat.—Before the examination can be commenced the fat must be prepared in a clear and dry condition. This may be done by melting 50 grms. or so in a small beaker and filtering through a coarse filter-paper (e.g., Whatman, No. 5) standing in a warm place—the top of the water-oven is very suitable. The fat so obtained should be perfectly clear and bright and should be well mixed before portions are drawn off for the various tests.

After solidification the fat should be always completely liquefied before portions are removed, to prevent any possibility of fractionation.

Examination under the Food and Drugs Acts.—Under normal circumstances it is not necessary to determine in detail the composition of a margarine fat bought as a sample under the Food and Drugs Acts. The only legal requirement as far as the composition of the fat is concerned (apart, of course, from unwholesome ingredients) is that it shall not contain more than 10 per cent. of butter fat—an adulteration by the addition of excess of butter fat is most unusual as it is not a commercial proposition under existing conditions, moreover, as it is not to the prejudice of the purchaser, it is merely a technical offence under Section 8 of the 1899 Act and not an offence under Section 6 of the main Act, so that a prosecution would only be likely where there was some evidence to show that the mixture had been prepared with the object of selling it as butter. The reasons for thus limiting the legal percentage of butter are summarised on page 415. The determination of the percentage of butter fat is therefore frequently necessary for this and for other reasons, such as the composition of supplies to hospitals, etc. The methods used and the calculations involved are given in detail below.

Determination of Butter Fat.—Butter fat is determined by the method of Kirschner (see page 154) the Reichert and Polenske values being necessary for purposes of the correct interpretation of the results obtained. The general principles of the method for calculating the proportion of butter from the results obtained are given on page 334 under the determination of coconut oil, the main point being that the Kirschner value for any given mixture is proportioned to the amount of butter contained therein. Where coconut oil and oils of a similar character are practically absent, i.e., where the Polenske is not more than 2·0, the amount of butter may be calculated from the formula:

$$\text{percentage of butter} = \frac{K - 0{\cdot}3}{0{\cdot}235}.$$

Where K is the Kirschner value of the mixture and 0·3 the average Kirschner given by a margarine containing no butter or oil of the coconut class. Where the Polenske value is more than 2 the right-hand side of the above equation must be corrected in accordance with the actual Polenske value found, as given in the following table:

Polenske.	Equation.
2·0–4·5	$\frac{K-P/6-0\cdot2}{0\cdot235}$
5·0–7·0	$\frac{K-P/6-0\cdot1}{0\cdot235}$
7·0–9·0	$\frac{K-P/7-0\cdot1}{0\cdot235}$
9·0–10·0	$\frac{K-P/8-0\cdot1}{0\cdot235}$
10·0–12·0	$\frac{K-P/10-0\cdot1}{0\cdot235}$
12·0–17·0	$\frac{K-P/10}{0\cdot235}$

The percentage of butter fat can also be calculated, but with a somewhat lower degree of accuracy, from the Reichert value from the equation:

$$\text{percentage of butter fat} = \frac{R-0\cdot065C-0\cdot2}{0\cdot284}.$$

Where R is the corrected Reichert value obtained as described on page 335.

The formula of Bolton, Richmond and Revis (*Analyst*, 1912, 37, 183) is somewhat simpler than the above, but for amounts of butter round about 1 per cent. is inclined to give somewhat high results:

$$\text{butter per cent.} = \frac{K-(0\cdot262P^{0\cdot63}+0\cdot09)}{0\cdot242},$$

or nearly as exactly by

$$\text{butter per cent.} = \frac{K-(0\cdot1P+0\cdot24)}{0\cdot244}.$$

The Determination of the "Fat-not-Butter" of Margarine.—The amount of coconut oil having been determined by the method given on page 334 and the butter as given above from a consideration of the Reichert, Polenske, Kirschner value (due care, of course, having been given to the distinction between coconut, palm kernel and other oils of the same family) it may be necessary to continue the examination for the detection and determination of the other constituents of the mixture if any are present. In the first place colour tests may be applied for sesamé and cotton-seed oils, the remarks on these tests, which may be found on page 80, being kept well in mind. Reasonable positive results may be taken as proof that the oils indicated are present, but mere traces may be disregarded. It should be remembered that a pure hog fat even when the animal has been fed on oil cake seldom gives a reaction for more than 5 per cent. of the oil in question so that such an animal fat when diluted in a margarine with other fats will only give the faintest reaction. A negative reaction for cotton-seed oil does not necessarily

show that this oil is absent. (Cf. pages 320 and 205 for tests for palm and maize oils.)

The first two determinations should be the iodine value and the refractive index. The amount of butter fat and coconut oil (or similar oil) present being known, the calculated values for these may be substituted and the values thus obtained for the remainder of the oils present. Vegetable oils will have higher iodine values than animal oils, whilst the presence of vegetable oils will be confirmed by a high refractive index. The saponification value is occasionally useful more particularly in the case of an oleomargarine (margarine free from butter and coconut oil), but as a general rule any information so obtained can be deduced from the other usual tests.

Where a high iodine value is obtained indicating the presence of liquid vegetable oils the results of the colour tests should be taken into account, and where there is a possibility of the presence of arachis oil an attempt should be made to isolate arachidic acid as explained on pages 260–262. Where there is any doubt as to the presence of a larger amount of the semi-drying or non-drying liquid oils or a smaller amount of the drying oils the problem may be simplified somewhat by the determination of the iodine value of the liquid fatty acids, but, unfortunately, the additional information so obtained seldom repays the trouble involved in the separation. (See iodine value, page 137, and separation of liquid fatty acids, page 45.) It may not always be possible to state definitely the exact liquid oils present, but it is usually comparatively simple to give the approximate quantity as a class. Settimj and Maurantonio (*Analyst*, 1913, 38, 21) suggest that the greater part of the vegetable oils present may be separated by heating a portion of the sample with rather more than its own volume of 95 per cent. alcohol, allowing to cool and decanting the alcoholic layer. On evaporating the alcohol much of the liquid oils and little of the animal oils will be obtained, the method, although useful, is by no means as absolute as these authors imply.

The animal fats (lard and beef fat) will be indicated from the melting-point of the margarine when taken in conjunction with the already known constituents of the mixture and the distinction between the two may be made by means of crystallising the fat from ether and examining the crystals obtained along the lines suggested for the presence of beef fat in lard (page 364) and beef and lard in butter (page 398). The presence of hydrogenated oils will simulate, in several of these tests, the presence of beef fat. The presence or absence of hydrogenated oils is not always an easy matter to decide, but careful consideration of the various results obtained and the special tests for nickel and " new-acids," described on page 471, will prove of value in arriving at a conclusion. Comparison should always be made with mixtures of known composition especially in the case of factors, such as the melting-point, which are not strictly additive. The following tables due to Clayton (*Margarine*, page 114) will assist in the elucidation of the composition of samples of margarine. The first table gives the composition of eight mixtures of fat prepared in the laboratory; the second table gives the analytical figures which were observed for these mixtures. The student should take the results given in the second table and work out from these the proportion of the ingredients likely to be present and compare the results so obtained with the actual composition of the mixture as given in the first table.

TABLE CCXXX.—COMPOSITION OF EIGHT MIXTURES OF FATS

Fatty Constituents.	A.	B.	C.	D.	E.	F.	G.	H.
Butter fat	..	10%	..	..	..	10%	10%	..
Oleo	55	50	..	30	..	..	..	60
Première jus	..	..	..	10	15	..	..	..
Coconut oil	25	25	50	25	15	70	35	..
Palm-kernel oil	..	..	30	..	50	..	35	..
Cotton-seed oil	10	5	..	20	20	20	20	10
Ground-nut oil	..	..	20	..	..	..	..	..
Lard	..	..	..	15	..	..	..	30
Hardened whale oil	10	10	..	..	..	..	..	..

TABLE CCXXXI.—ANALYTICAL VALUES FROM FOREGOING

Analytical Value.	A.	B.	C.	D.	E.	F.	G.	H
Reichert-Meissl No.	2·7	5·9	5·6	1·5	4·2	8·9	7·4	
Polenske No.	4·6	4·8	12·0	3·2	9·1	11·4	9·3	
Kirschner No.	0·8	2·74	1·5	0·5	0·8	3·7	3·7	
Total Blichfeldt No.	5·25	8·2	14·6	5·2	10·0	17·7	15·1	
Soluble „ „	0·85	3·2	2·2	0·8	1·86	4·9	4·6	
Insol. „ „	4·4	4·9	12·4	4·4	8·14	12·8	10·5	
Saponification value	212·0	214·3	242·7	210	234	242	234	19
Iodine value	47·71	42·17	29·1	56·1	34·1	32·2	34·0	5
Refractive index at 40° C.	46·0	46·0	40·0	46·8	43·0	40·0	40·8	4
Melting-point	27·3	28·8	20·7	23·6	24·8	20·5	21·8	2
Halphen test	++	+	–	+++	+++	+++	+++	
Belfield test (beef	+++	+++	–	+++	+++	–	–	+
Belfield test (lard	–	–	–	+	–	–	–	+
Nickel test	+	+	–	–	–	–	–	

Legal Requirements for Margarine.—The first special enactment in connection with margarine was contained in the Margarine Act of 1887 which was passed, as stated in the preamble, to make provision for protecting the public against the sale as butter of substances made in imitation of butter, as well as of butter mixed with any such substances. This act after defining margarine (the definition is quoted on page 404) states that no butter substitute shall be lawfully sold except under the name of margarine and further that " Every package, whether open or closed, and containing margarine, shall be branded or durably marked ' margarine ' on the top, bottom and sides, in printed capital letters, not less than three-quarters of an inch square; and if such margarine be exposed for sale, by retail, there shall be attached to each parcel thereof so exposed, and in such manner as to be clearly visible to the purchaser, a label marked in printed capital letters not less than one and a half inches square, ' Margarine '; and every person selling margarine by retail, save in a package duly branded or durably marked as aforesaid, shall in every case deliver the same to the purchaser in (or with) a paper

wrapper, on which shall be printed in capital letters (not less than a quarter of an inch square) ' Margarine.'

The word ' package ' in this section refers to the large 56 lb. wooden boxes in which margarine is ordinarily sold in bulk and does not refer to a sale by retail of, say, half a pound. The word ' parcel ' refers to the whole block or bulk when exposed for sale in a retail shop and may consist of a number of small packets resting on one another. The words ' or with ' are repealed by Section 6 of the 1899 Act and the words ' not less than a quarter of an inch square ' have been altered to ' capital block letters not less than half an inch long and distinctly legible and no other printed matter shall appear on the wrapper. . . .'

The Act also contains provisions for the registration of margarine factories, and this has been extended to wholesale dealers in Section 7 of the Sale of Food and Drugs Act, 1899, and has been extended by the Butter and Margarine Act, 1907.

The Sale of Food and Drugs Act, 1899, extends the provisions in regard to the sale of margarine to margarine cheese and limits the amount of butter fat lawfully present in the fat of margarine to 10 per cent. (see below).

The Butter and Margarine Act, 1907, refers to the registration of butter and margarine factories and their inspection. It lays down the limit for the percentage of water in butter or margarine as 16 per cent. and has the two following clauses : " If in any wrapper enclosing margarine, or on any package containing margarine, or on any label attached to a parcel of margarine, or in any advertisement or invoice of margarine a person dealing in margarine describes it by any name other than either ' margarine,' or a name combining the word ' margarine ' with a fancy or other descriptive name approved by the Board of Agriculture and Fisheries and printed in type not larger than and in the same colour as the word ' margarine,' he shall be guilty of an offence under this Act." " A name shall not be approved by the Board of Agriculture and Fisheries for use in connection with margarine if it refers to or is suggestive of butter or anything connected with the dairy interest, nor shall such a name be approved as a name under which milk-blended butter may be imported or dealt with."

It will be seen from a careful study of these two sections, together with Section 27 of the 1875 Act, that the sale of any substances described as " Butter mixture," " Margarine mixture," " Margarine mixed with Butter " is illegal, although a statement that " Elephant margarine is blended with pure butter," not being a name, would probably not be an offence under the label section of the 1907 Act. The latter description, however, would be an offence under Section 6 of the 1875 Act as a blend suggests that the substance blended affects the taste of the finished article and it would require, at the very least, 20 per cent. of butter to flavour seriously any margarine except a perfectly tasteless one. In any case where the product did contain this amount an offence would be committed under Section 8 of the 1899 Act, so that the sale of an article so described is obviously quite illegal.

At first sight it may not be easy to see the reason for restricting the amount of butter fat in margarine fat, yet the provision is, nevertheless, quite a wise one. Before the passing of the 1899 Act it was found that margarines were being prepared containing up to 80 per cent. of butter and it will be obvious that such a mixture although legally " margarine " has only a commercial advantage if sold as " butter " and was doubtless so intended to be sold. When such fraud was discovered the defence could always be that a mistake had been made and that the substitution was accidental.

When the 1899 Act was going through Parliament it was decided that,

in order to make substitution less likely, butter fat should be entirely excluded from margarine, but the manufacturers urged that a small trace of butter fat would always be present on account of the use of milk or separated milk during the course of manufacture and so they asked to be allowed a certain small percentage to cover this difficulty. An amount of 10 per cent. was suggested, an amount which was considered to be far in excess of anything likely to be present, in order to allow for all eventualities—at the time of the passing of the Act the idea that anyone would take advantage of the full 10 per cent. was never contemplated. No butter fat, as such, is used now except with the idea of using some such phrase as " contains the highest percentage of butter legally possible " so that the public, who, generally speaking, have no knowledge of the limit of 10 per cent., may be misled into thinking that the article in question is something different from margarine. The law on this subject may be summed up in a few words—if a given butter-like substance is not butter (or milk-blended butter) it is margarine.

CHAPTER XXVII

DAIRY PRODUCTS

Milk

Milk is the natural secretion of the mammary glands of the female mammal intended for the nourishment of the young. These glands are active over a more or less indefinite period immediately following parturition. The milks from different animals, although having similar general composition and characteristics, have various marked differences in the nature and amount of their constituents, and it is quite impossible to draw conclusions as to the milk of one type of animal from observations on that of another type.

The milk of the cow is by far the most important from the commercial point of view in this country and it has been studied in some detail—a large amount of work, however, still remains to be done before our knowledge of even this one can be considered at all complete. The milks of other animals have been studied to a much less extent and, comparatively speaking, very little is known of their constitution.

All milks are alike in that they consist of water, fat, proteins, sugar and mineral matter, but not only the amount of these varies within wide limits for different animals but also the actual members of these individual classes. The composition of the more important milks will be given below as far as it is more or less definitely known.

Cow's Milk

General Composition.—Cow's milk, like that of the milk of all other animals, being a natural product its composition, in so far as the proportions of its constituents are concerned, is subjected to variations depending upon various factors. The time and method of milking, the food of the animal and its environment, the weather conditions and the breed all influence to a certain extent the amount and proportion of the various constituents, but it may be taken as a well-established fact that, apart from the well-recognised seasonal variations and the effect of different intervals of milking upon the morning and evening milking, the milk supplied by a herd of good cows under fair average conditions will not vary very greatly from the following average composition as given by Richmond:

Water	87·34
Fat	3·75
Lactose	4·70
Casein	3·00
Albumin	0·40
Ash	0·75
Other constituents	0·06
	100·00

The maximum and minimum figures recorded for fats are 12·52 per cent.*

* Cf. Hodgson (*Analyst*, 1923, 48, 443). Fat, 19·50 per cent.

and 1·04 per cent. and for solids-not-fat, 10·60–4·90 per cent. The evening milk usually contains 0·2–0·7 per cent. more fat than the morning owing to the shorter time between milkings usual in the former case. The fat is usually at its lowest in May and June and at its highest in November. The solids-not-fat are frequently somewhat lower in July and August, particularly in a dry season.

It has been shown by Vieth that the average proportion between milk sugar, protein and ash in a normal milk is as 13 : 9 : 2, and this has been fully confirmed by Richmond and many other workers. A genuine milk abnormally low in solids-not-fat nearly always gives a very different ratio, and this is an almost certain method of distinguishing between an adulterated and an abnormal milk. Richmond suggests a multiple standard of 8·5 per cent. of solids-not-fat; 4·5 per cent. of milk sugar; 0·5 per cent. of total nitrogen (=3·19 per cent. of proteins); and 0·70 per cent. of ash. Ash insoluble in hot water should not be less than 0·50 per cent. "A milk should never be pronounced as watered on the evidence of the solids-not-fat alone—unless this is well below 8·0 per cent. A determination of the milk sugar, total nitrogen, and ash should be made in addition; a judgment formed on these three determinations will in all probability be correct, and if the figures for at least two of them are above the limit, the milk is probably genuine."

Richmond's table shows that the ash in abnormal milks never falls below 0·70 per cent., and that this may be taken as the lower limit. The proteins also remain practically constant at 3·4 per cent. irrespective of the amount of solids-not-fat, whilst the lactose varies from 4·9–4·0 per cent.

The average composition of cow's milk in England as judged by the analysis of hundreds of thousands of samples by Vieth and Richmond for the Aylesbury Dairy Company may be seen from the following table:

TABLE CCXXXII.—COMPOSITION OF MORNING AND EVENING MILK (1897–1916)

Month.	Morning Milk.				Evening Milk.			
	Specific Gravity.	Total Solids.	Fat.	Solids-not-fat.	Specific Gravity.	Total Solids.	Fat.	Solids-not-fat.
January . .	1·0323	12·59	3·65	8·94	1·0321	12·90	3·93	8·97
February . .	1·0324	12·52	3·57	8·95	1·0322	12·82	3·87	8·95
March . .	1·0323	12·46	3·52	8·94	1·0320	12·77	3·82	8·95
April . . .	1·0322	12·39	3·49	8·90	1·0320	12·69	3·81	8·88
May . . .	1·0325	12·28	3·34	8·94	1·0320	12·72	3·78	8·94
June . . .	1·0325	12·21	3·30	8·91	1·0320	12·63	3·75	8·88
July . . .	1·0320	12·24	3·47	8·77	1·0314	12·55	3·80	8·75
August . .	1·0317	12·32	3·56	8·76	1·0313	12·70	3·95	8·75
September .	1·0320	12·50	3·64	8·86	1·0316	12·89	4·05	8·84
October . .	1·0322	12·66	3·72	8·94	1·0319	13·02	4·10	8·92
November. .	1·0323	12·79	3·82	8·97	1·0320	13·09	4·14	8·95
December .	1·0323	12·74	3·77	8·97	1·0320	13·00	4·05	8·95
Average. .	1·0322	12·47	3·57	8·90	1·0319	12·81	3·92	8·89

G. C. Jones finds the average composition of milk for the years 1909–1918:

Month	Morning Milk.		Evening Milk.	
	Fat.	Solids-not-fat.	Fat.	Solids-not-fat.
January	3·62	8·95	3·91	8·95
February	3·54	8·95	3·84	8·94
March	3·49	8·93	3·80	8·93
April	3·43	8·89	3·76	8·87
May	3·31	8·92	3·76	8·91
June	3·26	8·91	3·74	8·87
July	3·40	8·81	3·80	8·75
August	3·49	8·79	3·94	8·74
September	3·61	8·86	4·05	8·84
October	3·71	8·93	4·11	8·92
November	3·82	8·96	4·14	8·95
December	3·77	8·94	4·02	8·94
Average	3·62	8·90	3·91	8·88

Total mean fat, 3·76; solids-not-fat, 8·89.

Similar figures have been obtained by the analysis of large numbers of samples taken under the Sale of Food and Drugs Acts, although, according to some authorities, there was, some years ago, distinct evidence of tampering in some districts. (Arnaud and Russell, *Analyst*, 1910, 35, 8.)

Colostrum.—Colostrum is the substance which is secreted by the animal before and immediately after parturition. This substance is much deeper in colour than milk and is usually thicker; it is easily curdled. Under the microscope colostrum exhibits numerous large clusters of cells, first observed by Donne and called by him "*corps granuleux*." Occasionally blood is present. The average composition of colostrum, according to Engling, is:

Water	71·69
Fat	3·37
Proteins	20·68
Sugar	2·48
Ash	1·78

Milk of Other Animals

As has been stated above, although the milk of all animals contains representatives of the same classes of substances, yet these representatives may differ widely. Thus, human milk, although containing sugar, proteins and fat as does cow's milk, has widely different properties from the latter. The sugar present is probably not lactose, the fat is practically devoid of volatile acids, and the proteins behave in a very different manner from those of cow's milk. In the following tables the composition of the milk of various animals is given—the table is due to Richmond:

TABLE CCXXXIII.—COMPOSITION OF MAMMALIAN MILK

	Water.	Fat.	Sugar.	Casein.	Albumin.	Ash.
	%	%	%	%	%	%
Cow	87·32	3·75	4·75	3·00	0·40	0·75
Goat	86·04	4·63	4·22	3·49	0·86	0·76
Ewe	79·46	8·63	4·28	5·23	1·45	0·97
Buffalo	82·34	7·57	4·96	3·62	0·60	0·84
Woman	88·5	3·3	6·8	0·9	0·4	0·20
Mare	89·80	1·17	6·89	1·84		0·30
Ass	90·12	1·26	6·50	1·32	0·34	0·46
Mule	91·50	1·59	4·80	1·64		0·38
Bitch	75·44	9·57	3·09	6·10	5·05	0·73
Cat	81·63	3·33	4·91	3·12	5·96	0·58
Rabbit	69·50	10·45	1·95	15·54		2·56
Llama	86·55	3·15	5·60	3·00	0·90	0·80
Camel	86·57	3·07	5·59	4·00		0·77
Elephant	67·85	19·57	8·84	3·09		0·65
Sow	84·04	4·55	3·13	7·23		1·05
Porpoise	41·11	48·50	1·33	11·19		0·57
Whale	48·67	43·67		7·11		0·46

ANALYSIS OF MILK

Specific Gravity.—This may be determined by means of a delicate hydrometer or a Westphal balance. The specific gravity of genuine milk generally falls between 1·029 and 1·034 at 15·5°. In case the gravity is taken at another temperature, it may be corrected by means of Richmond's table or the slide-rule. In correcting specific gravity for temperature it is generally sufficient to add or subtract 0·0002 for each degree over or under 15·5°.

The samples should be shaken gently just before taking the specific gravity, in order to mix in the cream, but care must be taken to avoid the formation of air bubbles.

The specific gravity of milk is raised by the abstraction of fat, and lowered by the addition of water; hence by partial skimming and watering an adulterated sample may possess the same gravity as that of genuine milk.

Total Solids and Ash.—About 5 grms. of milk are measured out into a weighed platinum, porcelain or nickel dish from a pipette, and the whole is again rapidly weighed. The dish is placed on a boiling water-bath until the solids are apparently dry, and then heated in the water-oven for three hours, cooled in the desiccator and weighed to obtain the total solids.

The ash is preferably estimated on at least 10 grms. of the milk. The solids are ignited at as low a temperature as possible, the flame (e.g., a luminous Argand burner) being placed some distance below the dish, to avoid volatilisation of chlorides.

When the milk is sour it should be neutralised to phenol-phthalein with N/10 caustic soda or strontia before evaporation, the weight of solids being corrected for the amount of alkali added. The total solids will be low on account of the production of valatile products during the decomposition, but suitable corrections may be made. (See Richmond and Miller,

Analyst, 1906, 31, 317; Richmond, *Dairy Chemistry*, 3rd edition, p. 319; compare also the maceration method for fat.)

Determination of Fat.—Röse-Gottleib.—For this the following reagents are required :

(1) Strong alcohol (95 per cent. by volume).
(2) A solution of ammonia (made by mixing 100 c.c. of 0·880 ammonia with 100 c.c. of water).
(3) Methylated ether, sp. gr. 0·720.
(4) Petroleum ether, distilling from 40°–60°, and leaving no residue.

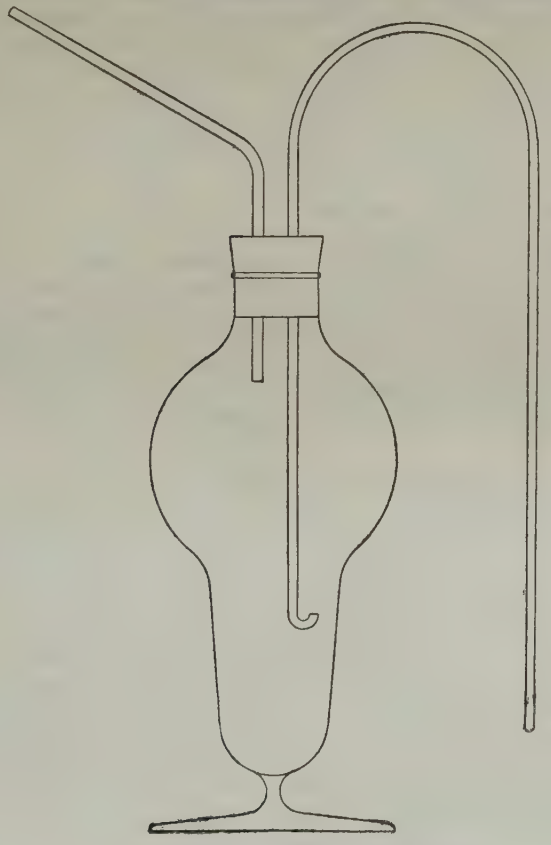

FIG. 9.—Eichloff and Grimmes' Apparatus
(E. R. Bolton)

[*By permission of J. & A. Churchill*

Apparatus.—A strong glass tube about $\frac{3}{4}$ inch in diameter and holding 50 c.c. fitted with an india-rubber stopper. Instead of this tube, the apparatus shown in Fig. 9 will be found of great advantage (Eichloff and Grimmes).

In the tube or apparatus are placed 5 grms. of milk, 0·5 c.c. of ammonia solution added, and the contents mixed by swinging the tube in a circular manner. Then 5 c.c. of alcohol are added, the whole again mixed, 12·5 c.c. of methylated ether run in and the stopper inserted. The tube is inverted three times, after which 12·5 c.c. of petroleum ether are run in and the tube again inverted three times (any violent shaking must be avoided). The

tube is allowed to stand and settle out; the ether solution is then blown off into a weighed flask, by means of a wash-bottle arrangement (shown in place in Fig. 9), down to $\frac{1}{4}$ in. from the aqueous layer. A fresh quantity of petroleum ether (or mixed ethers recovered from other tests) is run into the tube, and the contents mixed once by inversion. This ether is then blown off and the process repeated once more. The ether is then distilled off from the fat and the flask dried to constant weight in the water-oven. From this weight any residue insoluble in petroleum ether should be subtracted.

Some observers consider that a most thorough shaking is desirable which must be followed by the breaking down of the emulsion formed by means of the centrifuge. This would appear to be unnecessary, but in cases of doubt the residue in the apparatus may be acidified by the addition of an equal volume of concentrated hydrochloric acid and a further extraction with methylated ether. Any residue so obtained should be re-extracted with petroleum ether and any fat resulting added to that originally obtained.

Determination of Proteins.—By the Kjeldahl method using 10 grms. of milk.

$$\text{c.c. N/10 acid} \times 0{\cdot}014 = \% \text{ N}; \quad \text{c.c.} \times 0{\cdot}08932 = \% \text{ proteins.}$$

Determination of Milk Sugar.—Reduction Method.—10 c.c. of milk are made up to about 80 c.c. with water, just neutralised with N/10 NaOH and Fehling's solution A added drop by drop until a flocculent precipitate forms and settles, leaving a clear solution. The solution is then made up to 100·67 c.c., well mixed, and filtered (the 0·67 c.c. is to allow for the volume occupied by the proteins and fat). The process is then continued by the usual method. (Cf. *Analyst*, 1919, 44, 408.)

$$\% \text{ anhydrous lactose (approx.)} = \text{CuO} \times 0{\cdot}64.$$

Detection and Determination of Preservatives.—Boric Acid.—Detection.—A few drops of milk are placed in a depression in a spot plate, and one drop of turmeric tincture and a drop of dilute hydrochloric acid added. The tile is warmed on the water-bath until the milk is dry; in the presence of boric acid a pink colour will be developed.

Determination.—70 c.c. of milk are added to 7 c.c. of approx. 3N·NaOH in a 3 in. flat-bottomed platinum dish and evaporated on the water-bath, the skin which forms being periodically removed to the side. A flame is applied to the side of the dish, care being taken that the contents do not froth over; the ignition is completed at a high temperature until the ash is almost white. The dish is cooled, and 35 c.c. of water are added and allowed to stand until the melt is disintegrated, when it is filtered* into a 100 c.c. flask. 5 c.c. of approx. 3N hydrochloric acid and 15 c.c. of water are added to the dish and the solution again filtered through the same filter into the same flask. The dish is further treated with 4 c.c. of 3N hydrochloric acid and 10 c.c. of water and again filtered. To the mixed filtrates 7 c.c. of calcium chloride solution (10 per cent.) and phenol-phthalein are added, and then N/1 NaOH is added until a slight permanent pink colour is produced. The liquid is diluted to the mark and filtered into a graduated cylinder. 80 c.c. of the filtrate are made slightly acid to methyl orange with hydrochloric acid and boiled to eliminate carbon dioxide. The solution is cooled and titrated with N/10 sodium hydroxide until neutral to methyl orange. 30 c.c. of glycerol or 10 grms. of mannitol are added and the titration continued until the solution is neutral to phenol-phthalein. The acidity

* Filtration is not really necessary.

due to 30 c.c. of glycerol is determined and subtracted from the number of c.c. of N/10 sodium hydroxide used after the addition of the glycerol; the difference multiplied by 0·011 gives the percentage of boric acid in the milk. In case the amount of sodium hydroxide used exceeds 1 c.c., a portion of the boric acid will be precipitated together with the calcium phosphate. In this case the precipitate is washed with 25 c.c. of water through a hole made in the filter-paper, 5 c.c. of 3N hydrochloric acid, a further 25 c.c. of water, 0·5 c.c. of calcium chloride solution and phenol-phthalein are added to the filtrate, and the liquid titrated with N sodium hydroxide until just pink. The solution is diluted to 100 c.c. filtered, and 80 c.c. titrated as before. The amount of boric acid so found is added to that found in the first precipitation after making the necessary correction for dilution.

Formaldehyde.—Detection.—Hehner's reagent for the detection of formaldehyde is prepared by mixing 25 c.c. of 5 per cent. ferric chloride solution and 1 litre of concentrated sulphuric acid. 2–3 c.c. are placed in a small test-tube and about 5 c.c. of the milk added carefully so that it forms a layer above the acid. In the presence of formaldehyde a violet colouration will be produced on standing. It has been stated that the presence of nitrites interferes with this reaction (*Analyst*, 1912, 37, 155, 178), but Elsdon and Sutcliffe do not agree with this statement (*Analyst*, 1913, 38, 452).

If the Gerber method for the estimation of fat is used and ferric sulphate is added to the acid used, in proportion to the amounts indicated above, formaldehyde will produce a violet colouration on shaking the tube. If nitrates or nitrites are present, a bright golden-brown colour is produced (*Analyst*, 1913, 38, 452). Nitrites may be detected by adding 1 or 2 c.c. of Griess-Ilosvay solution to 5 c.c. of milk; a pink colour developing in less than a quarter of an hour indicates nitrites.

Determination.—In the method of Shrewsbury and Knapp (*Analyst*, 1909, 34, 12), the reagent is made by mixing 100 c.c. of concentrated hydrochloric acid with 1·6 c.c. of N/1 nitric acid. 10 c.c. of the freshly-made reagent are added to 5 c.c. of the milk in a test-tube, the mixture shaken vigorously and kept for ten minutes in a water-bath at 50°, and then rapidly cooled. As the violet colour produced varies in intensity according to the amount of formaldehyde present, the formaldehyde may be estimated by comparison with standards. If the colour obtained is deeper than that shown by six parts of formaldehyde per million of milk, the sample should be diluted with pure milk. The most delicate quantitative reaction is obtained with milks containing 0·2 to six parts per million of formaldehyde. In case nitrites are present 5 c.c. of the milk are treated with 0·05 grm. of urea and 1 c.c. of N/1 sulphuric acid, and the mixture heated in the boiling water-bath for two minutes and then cooled; the Shrewsbury and Knapp method may then be performed in the usual way on the resulting liquid (Monier-Williams).

Benzoic Acid.—Detection.—Benzoic acid and salicylic acid have been used as preservatives in milk. For methods for the detection reference should be made to the undermentioned papers :

Liverseege and Evers, *J.S.C.I.*, 1913, 32, 319; Revis, *Analyst*, 1912, 37, 346; Hinks, *Analyst*, 1913, 38, 555.

Salicylic Acid.—See Revis and Payne (*Analyst*, 1907, 32, 286).

Annatto.—See H. Lowe (*Analyst*, 1925, 50, 335) and A. D. Gardiner (*ibid.*, p. 550).

Condensed Milk

Condensed milk was formerly manufactured by concentrating milk, often under reduced pressure, with or without the addition of cane-sugar and packing the product in sealed tins. The unsweetened variety existed in two chief kinds in one of which, "Evaporated Milk," the concentration was about double that of an average milk and in the other about three times. The composition of these various brands as usually found is given in the following table:

	Approximate Composition.		
	Fat.	Solids-not-fat.	Sucrose.
Unsweetened full-cream milk	9–10%	23·5–27%	..
Unsweetened full-cream milk enriched with cream	12%	23–25%	..
Sweetened full-cream milk	9–10·5%	23·5–27%	38–42%
Sweetened machine-skimmed milk . .	0·5– 1·0%	25–29%	44–47%

Very full and detailed reports have been made to the Local Government Board (now the Ministry of Health) on these subjects, which reports should be consulted for more detailed information. (*Food Reports*, *No.* 13, 1923; *No.* 15, 1911; *No.* 21, 1914.)

The Public Health (Condensed Milk) Regulations, 1923, stipulate that condensed milk sold by retail in small packages shall be labelled in a particular manner and that it shall contain not less than the appropriate percentages of milk-fat and milk-solids as specified in the following table:

Table CCXXXIV.—Percentage of Milk Fats in Condensed Milks

Description of Condensed Milk.	Percentage of Milk Fat.	Percentage of all Milk Solids—including Fat.
1. Full cream, unsweetened . . .	9·0	31·0
2. Full cream, sweetened . . .	9·0	31·0
3. Skimmed, unsweetened . . .	..	20·0
4. Skimmed, sweetened	..	26·0

Patents have been taken out for the incorporation of foreign fats in condensed milks.

Dried Milk

Dried milk is the substance produced by suitable means on removing practically the whole of the water from ordinary milk. A very full report has been submitted to the Local Government Board (now the Ministry of Health) by Coutts, Winfield and the Government Laboratory. (*Food*

Reports, No. 24, 1918.) This report contains full descriptions of the processes employed and the methods of analysis which yield good results.

Analysis of Dried Milks.—A 15 per cent. solution may be made in water and the solution so obtained treated as an ordinary milk. Where the milk is not completely soluble, or merely as an alternative method, the analysis may be carried out directly on the powder. For the determination of fat 1 grm. diluted with 5 c.c. of water may be used for the Röse-Gottleib method; 2 grms. for moisture and ash, 2 grms. for proteins, and 1 grm. extracted with boiling water and made to 100 c.c. for sugar.

Jephcott. *Analyst*, 1923, 48, 529. "Estimation of Fat, etc., in Dried Milks."

Bacharach. *Analyst*, 1923, 48, 521. "Estimation of Lactose."

The Public Health (Dried Milk) Regulations, 1923, require that dried milk sold by retail in small packages shall be labelled in a particular manner and that it contain not less than the appropriate quantity of fat as specified in the following table:

TABLE CCXXXV.—PERCENTAGE OF FATS IN DRIED MILKS

Description of Dried Milk.	Minimum percentage of Fat.
1. Full cream	26·0
2. Three-quarter cream . . .	20·0
3. Half cream	14·0
4. Quarter cream	8·0

CREAM

Cream is the substance rich in fat which rises as a layer when milk is allowed to stand. Under modern conditions it is usually obtained by mechanical means, the separated milk usually containing 0·1 to 0·2 per cent. of fat. There is no legal standard for the fat content of cream, but an average commercial sample usually contains about 40–50 per cent. During the last few years forty samples of "cream" and "preserved cream" examined in the author's laboratory have contained from 23·0 to 62·0 per cent. of fat.

Analysis of Cream.—This is carried out in a very similar way to that of milk (v.s.). For total solids about 2 grms., for fat by Röse-Gottleib, 1 grm., and for ash, a fairly large amount, up to 10–20 grms.

Preservatives may be detected and determined as under milk. In the case of formaldehyde the cream should be diluted with milk of known purity. The use of preservatives in cream is controlled by the Public Health (Milk and Cream) Regulations, 1912 and 1917.

CHEESE

Cheese is produced by the action of rennet (an enzyme prepared from the gastric juices of the calf) on milk in large vats under suitable conditions of temperature, etc. The character of the cheese depends largely on the temperature used during its production and on the method adopted. The curd is pressed and allowed to ripen for several weeks. The ripening process is not thoroughly understood, but is dependent upon the action of micro-organisms and of the enzymes contained by them and also those present in

the original milk. Practically the whole of the fat contained in the milk is carried down with the precipitated protein, whilst the lactose remains in the whey. Cheese consists then, chiefly of protein and fat with small quantities of lactose and ash, together with any added salt. The following table gives the composition of the better known kinds of cheese according to various authorities:

TABLE CCXXXVI.—COMPOSITION OF CHEESE

Kind.	Water.	Fat.	Protein.	Lactic Acid. Lactose.	Ash.
Cream	20–58	37–90	2–16	0·2–1·2	0·3–3·4
Camembert	45–52	21–30	19–23	0·4	3·0–5·0
Neufchatel (Bondon)	34–55	21–42	9–16	1·5–7·0	0·7–7·0
Stilton	20–35	30–44	24–36	1·0–3·3	2·7–4·0
Cheddar	27–34	26–33	27–46	0·9–1·9	3·6–4·7
Cheshire	30–40	25 *–34	23–36	2·4	3·6–4·8
Gruyère	31–37	27–30	28–35	0·7–3·3	3·1–5·3
Roquefort	21–37	30–36	24–33	0·7–1·9	4·4–7·0 †
Skimmed milk	28–42	10–26	30–44	0·8–4·2	4·2–6·4 †

The composition of various kinds of cheese is treated by the following, among others: Camembert cheese (Buttenburg and Guth, *Analyst*, 1908, 33, 51); cream cheese (Cribb, *ibid.*, 1909, 34, 45); Dutch cheese (Cribb, *ibid.*, 1906, 31, 105; Van Rijn, *ibid.*, 1915, 40, 391); Roquefort cheese (Dox, *ibid.*, 1911, 36, 542); cream cheese.

The analysis of cheese is usually restricted to a determination of the water, fat, protein and ash—the other ingredients being determined by difference. As margarine cheeses and filled cheeses are by no means unknown it is necessary to examine the fat by the methods suggested under butter fat. From the nature of things, however, adulteration with small quantities of fat is not a commercial proposition so that the determination of the Reichert and Polenske values is usually all that is necessary. From a cheese containing an average amount of fat sufficient of this for the determination of the Reichert value may usually be obtained by cutting up a quantity of the cheese, placing it on a porcelain filter-plate resting in a funnel and allowing the whole to remain in the water-oven until sufficient fat has run through. Should it not be possible to obtain sufficient fat by this method, it will be necessary to extract with ether and dry the resulting fat in the water-oven, the latter process usually taking about one or two hours.

The Analysis of Cheese.—Determination of Moisture and Ash.—This may be carried out by drying 5 grm. of the sample, cut into very thin slices, at 105° until constant in weight; the addition of a small amount of absolute alcohol will assist the drying. The ash may be determined on the same portion, heating gently to not more than a dull red in the dark.

A method for the determination of chlorides in cheese is given by Cornish and Golding (*Analyst*, 1915, 40, 197), whilst some remarks on mineral coating are due to Hinks (*ibid.*, 1911, 36, 61).

Determination of Proteins.—By the Kjeldahl process using 1·5 to 2 grms. of cheese. The percentage of nitrogen multiplied by 6·38 gives the percentage of proteins.

* Seldom falls below 28—usually 30 or more.
† Muter gives figures up to 10 per cent. and beyond.

Determination of Fat.—By the Röse-Gottleib process on about 1 grm. of the finely-grated cheese.

The standard for fat in a whole milk cheese is at least 45 per cent. of the total dry matter (total solids) of the cheese. Some countries have adopted 50 per cent. as the standard.

Butter

Butter is the substance, containing practically the whole of the fat of the milk from which it is prepared, produced by the continual shaking or beating of milk. In this country the milk of the cow is alone used, but in Egypt, India and other Eastern countries those of the buffalo and other animals are used. (Cf. Ghee and Samna, *infra*.)

Originally the production of butter by churning was carried out on the small scale and entirely for the private use of the maker. Except under special circumstances this is no longer the case and the bulk of the world production is manufactured in creameries who collect the milk from farms (or have it delivered to them) and where it is converted into butter under cleanly and hygienic conditions. As far as this country is concerned a large proportion (probably more than half) of the butter consumed is imported. In 1914 about 200,000 tons were imported from all parts of the world but owing to the higher prices ruling of later years and the growth of the use of margarine this quantity is now greatly reduced—in 1918 and 1919 the quantity was only about 75,000 tons, but this has increased in more recent years.

The butter is usually produced by churning the cream which has been separated from the milk, although occasionally the milk itself is churned. Years ago the cream was removed from the milk after it had been standing, by hand-skimming, but this is now done by mechanical separators which are highly efficient and which remove practically the whole of the cream. Separated milk is defined by the Sale of Milk Regulations, 1912, as milk which contains not less than 8·7 per cent. of solids-not-fat.

The average composition is:

Fat	0·1 (to 0·3)
Lactose	4·9
Proteins	3·6
Ash	0·8
Water	90·6

When the butter is freshly produced it consists of a nodular mass which is then worked, usually on butter tables of various types, with the idea of removing excess of water and making the whole into one homogeneous mass. Salt is added here as a flavouring agent and also to act as a mild preservative—unfortunately other preservatives which are not so mild may also be added here although their presence, as judged by the number of samples without, would not seem to be necessary.

The liquid left in the churn which is known as buttermilk is very similar in composition to skimmed milk but it usually contains appreciable quantities of lactic acid on account of the acidity of the cream from which it is prepared. It has been pointed out by Hodgson (*Analyst*, 1919, 44, 229) that the addition of water before churning is considered by some to be necessary in order to bring the temperature within the optimum zone for churning. This author states that :

" In attempting to obtain some information with respect to the composition of buttermilk, the author was able to find only very few references; practically the only reference of any value was found in Richmond's *Dairy Chemistry*, which states that buttermilk ' differs only slightly in composition

from skimmed milk,' the following analyses being given : Prepared from sour cream, fat 0·5 per cent., solids-not-fat 7·85 per cent.; prepared from milk, fat 0·5 per cent., solids-not-fat 8·37 per cent.; prepared from sweet cream, fat 0·35 per cent., solids-not-fat 8·67 per cent.; prepared from separated milk, fat 0·1 per cent., solids-not-fat 8·93 per cent.; Richmond also states that it is very rare to find as much as 2 per cent. of fat and also that it may contain water or other substances added during the churning.

" Inasmuch as the above analyses differ very materially from those obtained in this laboratory, and as it is very important to the Public Analyst to know how much added water may be expected, the author thinks that it might be of interest to give the results obtained with samples of buttermilk taken for analysis under the Sale of Foods and Drugs Acts.

" Buttermilk is a staple food in many parts of the country, and it is essential that the fraudulent addition of water should be prevented. It is well known that temperature has a very important influence on churning; if the temperature is too high, the production of butter is retarded, while if it is too low, the solid butter grains enclose liquid fat, the best temperature being from 51° to 57° F. The inevitable result of this is that a certain amount of water is added in order to bring the temperature between those figures, and the vendor is therefore in a measure protected by Section 6, Sub-section 4 of the Sale of Food and Drugs Act, 1875, which states that an offence shall not be deemed to have been committed ' where the food is unavoidably mixed with some extraneous matter in the process of production.' The problem which arises is how much water may be said to have been unavoidably added during ' the process of production ' and how much has been added fraudulently.

" There are no cases on record of any decision on the point having been given by the High Court either in England or Ireland, but the High Court of Justiciary in Scotland, in Warnock *v.* Johnstone, held that Sub-section (4) of Section (6) covered the defendant where 30 per cent. of water was added to the sample.

" It has therefore been the practice in this laboratory to caution the vendors of samples containing over 25 per cent. of added water and less than 30 per cent. and to take legal proceedings in all cases where the added water exceeds 30 per cent.

" The amount of fat present in the sample, of course, depends on the efficiency of the churning operations, but rarely exceeds 0·6 per cent. where the operation is carried on even approximately in an efficient manner."

TABLE CCXXXVII.—PERCENTAGES OF FATS IN BUTTERMILK (HODGSON)

TABLE A

Percentage of Fat.	Number of Samples.	Percentage of Whole.	Percentage of Fat.	Number of Samples.	Percentage of Whole.
Under 0·1	nil	..	0·9–0·99	6	1·9
0·1–0·19	5	1·6	1·0–1·09	2	0·6
0·2–0·29	15	4·8	1·1–1·19	2	0·6
0·3–0·39	61	19·6	1·2–1·29	nil	..
0·4–0·49	81	25·9	1·3–1·39	1	0·3
0·5–0·59	64	20·5	1·4–1·49	1	0·3
0·6–0·69	33	10·6	1·5–1·59	2	0·6
0·7–0·79	20	6·4	1·6–1·69	1	0·3
0·8–0·89	16	5·1	1·7–1·79	2	0·6

TABLE B

Solids-not-fat.	Number of Samples.	Added Water.	Percentage of the Whole.
3·7–3·79	1	56·5–55·4	0·3
3·8–4·49	nil	55·3–47·2	..
4·5–4·59	1	47·0–46·0	0·3
4·6–4·79	nil	45·8–43·6	..
4·8–4·89	1	43·5–42·5	0·3
4·9–4·99	1	42·3–41·3	0·3
5·0–5·09	nil	41·2–40·1	..
5·1–5·19	3	40·0–38·9	1·0
5·2–5·29	nil	38·8–37·8	..
5·3–5·39	2	37·7–36·6	0·6
5·4–5·49	1	36·5–35·4	0·3
5·5–5·59	3	35·3–34·2	1·0
5·6–5·69	4	34·1–33·1	1·3
5·7–5·79	5	32·9–31·9	1·6
5·8–5·89	5	31·8–30·7	1·6
5·9–5·99	6	30·6–29·5	1·9
6·0–6·09	13	29·4–28·4	4·2
6·1–6·19	8	28·2–27·2	2·6
6·2–6·29	6	27·0–26·0	1·9
6·3–6·39	13	25·9–24·8	4·2
6·4–6·49	24	24·7–23·7	7·7
6·5–6·59	17	23·5–22·5	5·4
6·6–6·69	21	22·4–21·3	6·7
6·7–6·79	21	21·2–20·1	6·7
6·8–6·89	18	20·0–18·9	5·8
6·9–6·99	14	18·8–17·8	4·5
7·0–7·09	22	17·7–16·6	7·1
7·1–7·19	13	16·5–15·4	4·2
7·2–7·29	14	15·3–14·2	4·5
7·3–7·39	16	14·1–13·1	5·1
7·4–7·49	8	12·9–11·9	2·6
7·5–7·59	8	11·8–10·7	2·6
7·6–7·69	9	10·6–9·5	2·9
7·7–7·79	7	9·4–8·4	2·2
7·8–7·89	6	8·2–7·2	1·9
7·9–7·99	6	7·1–6·0	1·9
8·0–8·09	2	5·9–4·8	0·6
8·1–8·19	3	4·7–3·7	1·0
8·2–8·29	nil	3·5–2·5	..
8·3–8·39	1	2·4–1·3	0·3
8·4–8·49	3	1·2–0·1	1·0
8·5 and over	6	..	1·9

The following Table shows the average solids-not-fat and the corresponding amount of added water for the samples received during each month of the year:

TABLE CCXXXVIII.—AVERAGE "SOLIDS-NOT-FAT" AND ADDED WATER IN SAMPLES OF BUTTERMILK (HODGSON)

Month.	Number of Samples.	Average Solids-not-fat.	Added Water.
January	17	6·79	20·12
February	19	6·82	19·77
March	43	6·96	18·11
April	27	7·10	16·47
May	22	6·89	18·94
June	43	6·88	19·06
July	18	6·57	22·71
August	19	7·02	17·42
September	22	7·03	17·30
October	10	6·71	21·06
November	32	6·60	22·35
December	40	6·92	18·59

The curd and whey from whole milk have the following average composition:

TABLE CCXXXIX.—COMPOSITION OF AVERAGE CURD AND WHEY

	Curd per cent.	Whey per cent.
Water	50·0	92·94
Fat	26·7	0·35
Sugar	2·3	5·10
Casein	20·0	0·46
Albumin	trace	0·46
Ash	1·0	0·69
	100·0	100·00

The following composition of buttermilk from sweet cream is given by Storch:

Water	89·74 per cent.
Fat	1·21 ,, ,,
Milk-sugar	4·98 ,, ,,
Protein	3·28 ,, ,,
Ash	0·79 ,, ,,

Buttermilk from ripened cream has the following composition:

TABLE CCXL.—COMPOSITION OF BUTTERMILK FROM RIPENED CREAM

Authority.	Storch.	Vieth.	Fleischmann.
	Per cent.	Per cent.	Per cent.
Water	90·93	90·39	91·24
Fat	0·31	0·50	0·56
Milk-sugar	4·58	4·06	..
Lactic acid	(?)	0·80	4·00
Protein	3·73	3·60	3·50
Ash	0·81	0·75	0·70

Richmond finds the following figures in buttermilks prepared in different ways:

TABLE CCXLI.—COMPOSITION OF BUTTERMILKS PREPARED IN DIFFERENT WAYS

	Sour Cream.	Sweet Cream.	Milk.	Separated Milk.
Specific gravity	1·0314	1·0331	1·0329	1·0355
Water	91·61	90·98	91·13	90·77
Fat	0·50	0·35	0·70	0·10
Sugar	3·40	4·42	3·65	3·93
Lactic acid	0·50	0·01	0·76	0·56
Protein	3·30	3·51	3·28	3·65
Ash	0·65	0·73	0·68	0·79

This author has found the amount of fat in buttermilk to vary from 0·15 per cent. to 5·60 per cent.; the last percentage is very unusual, and it is rare to find even as much as 2·0 per cent., percentages higher than this denoting that the churning has been carried out inefficiently.

It is sometimes asserted that a certain amount of water (20 or 25 per cent.) is allowed to be added to milk or cream for churning purposes. This view, however, appears to be quite incorrect; the addition of "breaking" water does not appear to be recognised by any statute, and if buttermilk is to be sold there is no reason why it should contain any added water. It is probable, however, that should a sample of buttermilk taken under the Sale of Food and Drugs Acts be found to contain a small percentage of added water, the Public Analyst would advise his authority that it is a custom sometimes to add a little water during churning, and a prosecution for the addition of small percentages is improbable.

The Analysis of Butter.—In determining the composition of a butter, determinations are usually made of water, curd, salt, ash and preservatives and fat—the latter being frequently determined by difference. The fat is,

of course, the valuable constituent and many workers think that a standard for the amount of fat would be far more valuable than the one for moisture which we now have; but this suggestion has not yet, however, been adopted officially although manufacturers of margarine have adopted it (cf. page 410).

Determination of Moisture.—Various routine methods such as those of Gerber, Stokes, etc., have been suggested, but for all ordinary purposes a convenient and quite accurate method is to weigh about 2 grms. into a flat-bottomed metal dish and heat for two hours on the boiling water-bath. The loss in weight indicates moisture.

Determination of Solids-not-fat.—The residue from the moisture determination may well be used for this. Ether is added to the dish to dissolve the fat which is decanted off through a small filter-paper taking care not to disturb the insoluble matter. When the solids have been washed free from fat by several quantities of ether, the residue is dried and weighed after any small portions which have inadvertently been carried on to the filter-paper have been returned. The salt may be titrated in the residue with silver nitrate solution in the usual way after ignition.

Preservatives.—The only usual preservative in butter, apart from salt, is a borax compound. This may be determined as follows: 6·2 grm. of butter are weighed out into a 250 c.c. wide-mouthed flask. About 50 c.c. of water are added and a few drops of litmus solution. The whole is then made acid with a few drops of N/10 hydrochloric acid, and boiled for a few minutes to eliminate carbon dioxide. The solution is cooled, neutralised to litmus with N/10 caustic soda, about 20 c.c. of glycerol or 10 grms. of mannitol added, and the titration continued until neutral to phenolphthalein. Each c.c. of soda used (allowing for any acidity due to the glycerol) after the addition of the glycerol, is equivalent to 0·1 per cent. of boric acid in the butter. This method tends to give results 0·05 per cent. too high.

The Composition of Butter.—Butter being a manufactured product prepared from a natural substance is obviously liable to fluctuations in its composition and will vary in character according to the source of the raw material and the manner of its preparation. The knowledge of this subject available up to the year 1900 is largely contained in the reports of the Departmental Committee for the Butter Regulations, and is well summarised in their final report issued in December 1903. This committee dealt with a whole mass of evidence and as a result made certain recommendations, some of which have been officially adopted.

The Proportion of Water in Butter.—As a result of their labours the Departmental Committee came to the conclusion that with the exception of one class of butter (that known as Irish Salt Firkin butter) it was not necessary to have the presence of more than 16 per cent. of water, and that this figure should be considered as the maximum allowable. It is generally agreed that this figure is quite high enough and in actual practice it is not often obtained. In recent years the writer has examined 700 samples of butter in which the moisture has varied from 7·0 to 16·9, the average being about 13·5 and only 0·9 per cent. being above the 16 per cent. limit.

The Non-Fatty Solids of Butter.—The non-fatty solids of butter consist almost entirely of the solids-not-fat of the milk, together with any salt which has been added during its preparation, and also, of course, the preservatives, if any.

König has summarised the analyses of some 300 samples of butter from various sources in the following table:

TABLE CCXLII.—SUMMARY OF ANALYSES OF 300 SAMPLES OF BUTTER (KÖNIG)

	Water.	Fat.	Casein.	Milk Sugar.	Lactic Acid.	Salts.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Minimum	4·15	69·96	0·19	0·45	..	0·02
Maximum	35·15	86·15	4·78	1·16	..	15·08
Mean	13·59	84·39	0·74	0·50	0·12	0·66

Vieth gives the following average results for butters of different origin:

TABLE CCXLIII.—COMPOSITION OF BUTTERS (VIETH)

Designation.	Fat.	Water.	Curd.	Salt.	$\frac{\text{Curd}}{\text{Water}} \times 100$.
	Per cent.	Per cent.	Per cent.	Per cent.	
English	86·85	11·54	0·59	1·02	5
French, fresh	84·77	13·76	1·38	0·09	10
,, salt	84·34	12·05	1·60	2·01	13
German, salt	85·24	12·24	1·17	1·35	10
Danish ,,	83·41	13·42	1·30	1·87	10
Swedish ,,	82·89	13·75	1·33	2·03	10

The following table gives the average composition of butter according to the various authorities. (Cf. *Report of Departmental Committee.*)

TABLE CCXLIV.—AVERAGE COMPOSITION OF BUTTERS

	Storch.		Mitchell.	Parry.	Richmond.	
	Fresh Cream.	Ripened Cream.			French.	Australian.
Fat	83·75	82·97	84–87	86·8	83·92	84·50
Water	13·03	13·78	12–14	12·0	14·33	12·70
Protein	0·64	0·84	0·75	0·5	1·36	1·21
Sugar	0·35	0·39	..	0·45	..	..
Ash	0·14	0·16	0·60	0·25	..	..
Salt	2·09	1·86	..	..	..	1·57
Lactic Acid	..	..	0·50	..	..	..

(Cf. Crowther, *Report No.* 66 *of the University of Leeds and the Yorks Council for Agricultural Education.*)

From the above results it will be seen that the solids-not-fat natural to butter (that is the total solids-not-fat less the salt) are not usually more than about 1·5. Figures greatly in excess of this would point to the artificial addition of milk solids which is sometimes done to enable the butter to hold more water without having an appearance of wetness. Richmond

(*Analyst*, 1906, 31, 177) has examined a substance sold for this purpose which had the following composition:

	Per cent.
Water	65·47
Fat	0·08
Sugar	2·24
Soluble proteid	0·69
Ash	1·02
Casein (by diff.)	30·50

He gives it as his opinion that any butter containing more than 2 per cent. of curd should be looked upon with suspicion; this is certainly, in general, a safe margin to adopt, although a few genuine samples have been known where the figure for curd has been much higher than this.

Miller has shown (*Analyst*, 1912, 37, 50) that the proportion of Protein may be calculated from the aldehyde figure using 10 grms. of butter.

Preservatives.—Although salt is not usually classed as a preservative in the somewhat restricted sense in which this word is usually employed, it nevertheless has undoubtedly some action in increasing the keeping properties of butter. (Some very interesting and possibly entertaining remarks on this subject will be found in the *Minutes of Evidence to the Interim Report of the Butter Committee*, pages 131 to 135, questions 4013–4125.) Other substances are frequently present however, the most common being borax or boric acid or a mixture of the two, while formalin, sulphites, fluorides, saltpetre, benzoates and salicylates have been used to a greater or less extent.

The extent to which a boron preservative has been used may be gathered from the following table which gives the results obtained with samples of butter taken in Salford under the Sale of Food and Drugs Act in recent years:

TABLE CCXLV.—PERCENTAGE OF PRESERVATIVE

Amount.	Number of Samples.	Percentage of whole.
Over 0·5%	5	0·6
0·41–0·5	9	1·1
0·31–0·4	12	1·5
0·21–0·3	22	2·7
0·11–0·2	41	5·0
0·01–0·1	86	10·4
Absent	649	78·8
	824	100·0

CHAPTER XXVIII

MARINE OILS

A COMPLETE account of the marine oils scarcely comes within the purpose of this book but as these products have been largely used as substitutes and adulterants and as a few of them, such as cod-liver oil, are of the first importance from the medicinal standpoint, some account of them is necessary. This group may be conveniently divided into three sub-groups which consist respectively of:

1. Fish oils.
2. Liver oils of certain fish.
3. Blubber oils from marine mammals.

All three classes usually convey the evidence of their source by taste and smell, although, of course, it is now possible to produce quite odourless and colourless solid fats from them by means of the process of hydrogenation. (Cf. C. K. Kutgen, *J.S.C.I.*, 1916, 35, 186.) The main point of difference between these oils and the vegetable oils is the presence in the former of highly unsaturated acids, one of which, named clupanodonic acid by Tsujimoto, may be converted into stearic acid by the addition of eight atoms of hydrogen. Further, they have high iodine values and absorb comparatively large quantities of oxygen, yet they do not give an elastic skin on drying as the drying vegetable oils do.

Various colour tests have been suggested for the recognition of this type of oil. The only one which is of much value is the sulphuric acid test which is fully described on page 77; most other tests are valueless (cf. Holde, *J.S.C.I.*, 1890, 9, 419; Lewkowitsch, *ibid.*, 1894, 13, 617).

The amount and biological significance of the fat in fish has been considered by O. Polimanti (*J.S.C.I.*, 1915, 34, 878), who finds that in general the bodies of fish which live at the surface of water contain a larger amount of fat than the bodies of those living in deep water or in the sand.

Eisenschiml and Copthorne (*Analyst*, 1910, 35, 249) base a test for fish oils in vegetable oils on the insolubility of the bromides of the former in chloroform. They work as follows :

About 5 c.c. of the oil to be tested are dissolved in 3 c.c. chloroform and 3 c.c. of glacial acetic acid, and bromine is added slowly drop by drop until the brown colour remains. After ten to fifteen minutes the vessel containing the mixture is placed in boiling water. Vegetable oils give a clear solution almost immediately, while oils containing even 5 per cent. of fish oil remain cloudy. The amount of fish oil present is stated to be roughly proportional to the weight of the precipitated bromides, but different specimens of the same class of fish oil vary greatly in their yield of insoluble bromides. Fish oils previously heated at or beyond 260° do not respond to this test.

In the case of boiled linseed oil it is necessary to remove metals before applying the test, by shaking the warm oil with warm 10 per cent. nitric acid saturated with potassium nitrate, and filtering the oil through paper till all moisture is removed.

A similar reaction has been proposed by Tortelli and Jaffe (*J.S.C.I.*, 1914, 33, 1061; 1915, 34, 1102). In their second paper they state that fish oils may be detected in vegetable oils by brominating 0·3 grm. of the unsaturated fatty acids (obtained by the lead-salt-ether method) in the cold (in acetic acid solution) and allowing to stand three hours; the liquid is then filtered and the bromide precipitated by adding a mixture of alcohol, ether and acetic acid; if the precipitated bromide leaves an insoluble residue on boiling with bromine water fish oil is present. A more simple method is to shake 10 c.c. of the mixed fatty acids with a mixture containing bromine 1, acetic acid 28, nitrobenzene 4, water 167 vols.; if no insoluble bromide is deposited after standing for 1 hour the oil is free from fish oil or from oils containing linolenic acid. If an insoluble bromide is obtained, it is filtered off and boiled with benzene for ½ hour; any insoluble bromide having a M.Pt. over 200° indicates the presence of fish oil. The colour reaction suggested by these authors in their former paper has been adversely criticised by J. Davidsohn (*ibid.*, 1916, 35, 186) and by M. Tsujimoto (*ibid.*, 1916, 35, 262).

Fish Oils

The principal fish oils which are on the market in any quantity are menhaden, sardine, salmon, herring and a mixture of oils known as Japan fish oil consisting of varying quantities of the oils of Japanese sardines and herrings. Some notes on the sources and composition of these oils are given here, whilst the usual characteristics are given in the table placed at the end of each section.

Menhaden Oil.—Menhaden oil is obtained from the body of the fish *Alosa menhaden*. This fish, which is largely found in American waters, resembles a herring although as a rule it is somewhat larger. The industry has now grown to considerable proportions on the Atlantic coast of America, the fish, after being cut up, being treated with steam in automatic conveyors when the oil separates out and is removed by settling. The residue is a valuable fertiliser. The fish contain varying amounts of oil, but it does not generally exceed 15 per cent. The better qualities are bleached by fuller's earth—inferior grades are obtained from putrid fish or by pressure from the residue.

The composition of menhaden oil was studied to a certain extent by Bull, who did not, however, come to any final conclusions beyond finding a certain proportion of fatty acids having a very high iodine value.

E. Twitchell (*J.S.C.I.*, 1917, 36, 892) has also examined the fatty acids of this oil and found them to be composed of palmitic acid 22·7, myristic acid 9·2, stearic acid 1·8, unsaturated C_{18} acids 24·9, unsaturated C_{20} acids 22·2, unsaturated C_{22} acids 20·2. Fusion of the fatty acids with potassium hydroxide did not yield arachidic acid, and hence the fatty acid with 22 carbon atoms was not erucic acid,* although, like that acid, it yielded behenic acid on hydrogenation. It is probably a more unsaturated acid, which is converted in the fusion into stearic or palmitic acid. This was confirmed by the depression of the M.Pt. of this fraction when melted with pure stearic and palmitic acids.

Brown and Beal (*J.S.C.I.*, 1923, 42, 665A) have continued this work recently in a long paper the abstract of which, as it is the best work on this oil up to the present, is given here *in extenso :*

" The mixed fatty acids of menhaden oil undergo an increase in molecular weight, as shown by titration, when heated at 240° in a current of carbon

* Cf., however, page 30.

dioxide, but the esters can be distilled almost without decomposition. Menhaden oil was esterified by means of alcoholic hydrogen chloride, and the ester, after distillation, treated with bromine in ethereal solution at $-10°$ to $-5°$. The percentage yield of bromide (polybromide number), and its bromine content were determined. The methyl ester, b.p. 195°–240° at 15 mm., has polybromide number 38·3, Br 68·31 per cent. (calculated for methyl clupanodonate, Br 68·79 per cent.). The ethyl and *n*-butyl esters and their bromo-derivatives were also prepared. That substitution does not occur is probable since the *n*-butyl ester from linseed oil, b.p. 190°–240° at 15 mm., gives a bromide M.Pt. 160° (polybromide number, 51·0), Br 59·30 per cent., evidently *n*-butyl hexabromostearate, for which Br = 59·38 per cent. Debromination of the bromides of the lower-boiling fractions of the ethyl esters of menhaden oil, by means of zinc and alcohol, gives an ester, iodine value 333, from which an acid, iodine value 342, molecular weight 305, is obtained on hydrolysis. It is, therefore, evident that a pure ester of clupanodonic acid ($C_{18}H_{28}O_2$) is not obtained in this way. Analytical data are given to show that the methyl esters of menhaden oil fatty acids may be partially separated by distillation into fractions, varying in boiling-point between 156°–166° at 15 mm. and 255°–260° at 15 mm., which are probably derived from acids of the C_{14}, C_{16}, C_{18}, C_{20}, and C_{22} series. Treatment of the lead soaps of menhaden oil by means of ether, and decomposition of the separated portions, give solid and liquid acids, but the methyl esters derived from the latter are also only partially separated by distillation. Separation of the barium soaps by means of benzene containing moist alcohol gives a liquid mixture of acids, of molecular weight varying between 255·2 and 336·7, from which methyl esters are obtained probably containing methyl arachidonate, methyl docosapentenoate, and perhaps methyl docosahexenoate. The most complete separation is effected by reducing the polybromides by means of zinc and methyl alcohol, and fractionally distilling the product. A fraction is obtained which is believed to be pure methyl clupanodonate, b.p. 215° at 15 mm., $n^{20} = 1·4860$, iodine value 348·8. The corresponding bromide, methyl octobromostearate, is a white, amorphous solid, M.Pt. 240°. In other fractions the presence of methyl arachidonate, methyl eicosapentenoate, methyl docosatetrenoate, methyl docosapentenoate, and methyl docosahexenoate seems probable. Exactly similar results are obtained starting from cod oil or herring oil. Unsaturated acids were obtained by the hydrolysis of the unsaturated esters derived from the polybromides. These were brominated, giving liquid and solid bromides, which were separately reduced, and again brominated. By analyses made at each step, it is shown that the liquid bromides contain less bromine than the solid bromides, and that, on reduction, the former give a product having an iodine value lower than that of the original acid, whilst the molecular weight is only slightly less. This product, on re-bromination, yields only a small amount of solid bromides. Since the degree of unsaturation decreases, structural change evidently occurs. Probably either a double bond migrates to the α-β-position in respect to the carboxyl (or ester) group, or a double bond may disappear by ring formation, as from a 1·5-diene grouping."

The following test has been proposed by A. Hoppenstedt (*J.S.C.I.*, 1911, 30, 36) for the detection of menhaden oil in cod-liver oil :

5 c.c. of the oil are dissolved in 5 c.c. of acetone in a test-tube of about 5/8 in. diameter, 1 c.c. of concentrated hydrochloric acid is added, and the whole shaken vigorously. 5 c.c. of petroleum ether are next added, and after mixing and allowing to separate, the colour of the acid layer is observed. With pure menhaden oil an intense bluish green is produced; with pure

cod-liver oil the layer assumes a yellow or brown colour, with no trace of green or blue. With a mixture of equal parts of menhaden oil and cod-liver oil the green colour is apparent, but is partially masked by the brown colour. The green colour can be observed when the quantity of menhaden oil is not less than 20 per cent., but below that point the green colour is almost completely masked by the brown due to the cod oil.

Too much reliance must not be placed on any such test as this. Menhaden oil has been used in large quantities as a substitute for, or an adulterant of, linseed oil, but like other fish oils it is greatly inferior to this. It is itself liable to adulteration with rosin oil and mineral oil—these may be detected by the determination of the unsaponifiable matter (not usually over 1·5 per cent., but E. W. Mann (*J.S.C.I.*, 1903, 22, 1357) has reported a sample as containing 6·7 per cent.) and the application of the Liebermann-Storch test.

Table CCXLVI.—Characteristics of Menhaden Oil

Specific gravity	0·928–0·933
n^{40}	1·4730–1·4736
Iodine value	150–180 *
Saponification value	190–195
Acid value	3·5–12·0
Unsaponifiable matter	0·6–1·6

(Cf. J. F. Liverseege, *Analyst*, 1904, 29, 211; J. Lund, *J.S.C.I.*, 1914, 33, 756; Brown and Beal, *ibid.*, 1923, 42, 665A.)

Sardine Oil.—This oil is prepared from the refuse obtained from canned sardines (*Clupea sardinus*, L.) at various places on the French and Spanish coasts. The oil may also be prepared from Indian sardines (cf. *J.S.C.I.*, 1914, 33, 491) and from Japanese sardines (*Clupanodon melanosticta*) the compositions of which are similar to that of the European fish.

The composition of the fatty acids of sardine oil has been considered by W. Fahrion (*J.S.C.I.*, 1893, 12, 938). He found that only small quantities of stearic acid were present and that the solid acids consisted for the most part of palmitic acid. He stated that the liquid unsaturated acids consisted mainly of jecoric acid $C_{18}H_{30}O_2$, an isomer of linolenic acid. Weiss (*ibid.*, 1893, 12, 937) took serious objection to these results. M. Tsujimoto (*Analyst*, 1906, 31, 335) from an examination of Japanese sardine oil found about 14 per cent. of a new fatty acid of the series $C_nH_{2n-8}O_2$, which he termed clupanodonic acid and to which he assigned the formula $C_{18}H_{28}O_2$, but which Majima and Okada (*J.S.C.I.*, 1914, 33, 362) suggested might be $C_{20}H_{32}O_2$ or even $C_{22}H_{36}O_2$. Fahrion repeated his work (*ibid.*, 1918, 37, 630A) and, although he confirmed the presence of clupanodonic acid, states that jecoric acid is present and also probably a less unsaturated fatty acid. In later papers Tsujimoto (*ibid.*, 1920, 39, 825; 1922, 41, 719A; 1923, 42, 1185A; cf. *Analyst*, 1921, 46, 57 and Goldschmidt and Weiss, *J.S.C.I.*, 1922, 41, 473A) state that the correct formula of clupanodonic acid is $C_{22}H_{34}O_2$ and that Japanese sardine oil probably also contains acids having the formulæ $C_{18}H_{28}O_2$ and $C_{20}H_{32}O_2$ ($C_{20}H_{30}O_2$ (?)) but that they have not yet been isolated. (Cf. S. Schmidt-Nielsen, *ibid.*, 1922, 41, 300A.) This latter formula has been confirmed by Eibner and Semmelbauer (*ibid.*, 1924, 43, B986; cf. Tsujimoto and Kimura, *J.S.C.I.*, 1924, 43, B62).

* Doubtless depends on method of preparation. A figure of 192·9 has been reported by Lewkowitsch.

Japanese sardine oil (also known as Japanese fish oil and which should be carefully distinguished from Japanese cod-liver oil) is prepared on the large scale sometimes by chopping up the fish and steaming, and sometimes by allowing the fish to rot when a portion of the oil can be separated, the remainder being obtained from the residue by pressure. By these methods various grades of oil are obtained. Frequently the Japanese oil is mixed with herring oil and sometimes with other fish oils. The analytical characteristics for the commercial oils are, therefore, kept separate in the table below.

A ten-years-old sample of sardine blubber, which formed a viscous brownish-yellow oil depositing crystalline fats at ordinary temperature, was examined by Eibner and Semmelbauer (*J.S.C.I.*, 1924, 43, B986). The characteristics of this were: iodine value, 136·0; acid value, 18·8; ester value, 179·8; saponif. value, 194·9; unsaponifiable matter, 0·5 per cent.; ash. 0·18 per cent. It contained clupanodonic acid, 12·7 per cent.; α-linoleic acid, 9·8 per cent.; isolinoleic acid, 10·1 per cent.; oleic acid, 28·6 per cent.; hydroxy-acids, 8·7 per cent.; saturated acids, 22·0 per cent.; glycerol, 4·1 per cent.; and cholesterol, 0·5 per cent. These authors state that the oil is not suitable as a drying oil for paints.

TABLE CCXLVII.—CHARACTERISTICS OF SARDINE OILS

	[4] European Oil.	[1] Malabar Oil.	[3] Commercial Japanese Oil.	[2] Japanese Oil.
Specific gravity	0·928–0·933	0·933–0·934	0·916–0·934	0·932–0·935
Acid value	4·6–21·7	0·5–26·0	10·0–40·0	1·3–8·2
Saponification value	189·0–193·0	192·2–195·0	189·8–192·0	194·8–196·2
Iodine value	192·0–193·0	154·0–172·0	121·0–171·0	180·6–187·3
n^{40}	..	1·4726–1·4736	1·4633–1·4665	1·4729–1·4735
Insoluble bromides	..	27·2–44·6	..	..
Unsaponifiable matter	0·5–1·4	1·8	0·5–1·5	..

[1] Sudborough, Watson and Kurup, *J.S.C.I.*, 1923, 42, 561A. [2] Tsujimoto, *Analyst*, 1906, 31, 335. [3] Fryer and Weston, *Oils, Fats and Waxes*, i, 101. [4] Fahrion. Some samples had iodine values as low as 161.

TABLE CCXLVIII.—CHARACTERISTICS OF FATTY ACIDS

	European Oil.	Malabar Oil.	Commercial Japanese Oil.	Japanese Oil.
Melting-point, °C.	..	..	..	35·4–36·2
Titre, °C.	..	30·6–33·4	28–	..
Neutralisation number	..	194–195	..	..
Insoluble bromides per cent.	..	..	..	44·2–47·1

Salmon Oil.—This oil is obtained in considerable quantities as a by-product of the British Columbia canning industry. The properties of the oil depend, as has been shown by Bailey and Johnson (*Analyst*, 1919, 44, 98), to a certain extent upon the particular type of salmon from which the oil is obtained. These authors obtained the following results for the iodine and insoluble bromide values:

	Iodine Number.	Hexabromide Value.
Chinook . . .	127–134	23–31
Chum	133–136	28–30
Red	141–148	33–37
Coho	153–156	43–46
Pink	154	40
Medium red . .	161–166	48–59

The following characteristics have been observed for various oils by different observers:

TABLE CCXLIX.—CHARACTERISTICS OF SALMON OIL

	[1] Red Salmon.	[2] King Salmon.	[2] Silver Salmon.	Commercial Oils.	
Specific gravity . .	0·925	0·927	0·918	[3] 0·926	[4] 0·924
Acid value . . .	7·4	9·8	..	..	45·5
Saponification value.	186·4	183·0	193·3	182·8	188·5
Iodine value . .	148·1	159·0	150·6	161·4	168·0
n_D^{40}	1·4701	1·4734	1·4698	1·4720	1·4713
Solidifying-point °C.	below −10	..	−3 to −11	..	..
M.Pt. of fatty acids °C.	26–28·5	..	..	..	..
Insoluble bromide value	38·9	..	45·0		..
Unsaponifiable matter	..	..	1·69	..	..
Titre °C. . . .	..	..	29·2	..	24·5

[1] S. Nakatogawa, *J.S.C.I.*, 1918, 37, 707A. [2] H. A. Gardner, *ibid.*, 1920, 39, 494A. [3] de Greiff, Iodine value of liquid fatty acids, 197·4. Reichert value, 0·6. [4] Fryer and Weston, *Oil of Rank Odour.*

Herring Oil.—This oil may be obtained from several species of herring, the commercial oils usually being those from the Norwegian herring (*Clupea harengus*) or the Japanese variety (*C. pallasi*). Bull, in an examination of this oil (*Chem. Zeit.*, 1899, 23, 996), states that he found unsaturated acids of the formulæ, $C_{20}H_{32}O_2$ and $C_{24}H_{40}O_2$ but this was not confirmed by M. Tsujimoto (*Analyst*, 1906, 31, 344) who, however, found 3·8 per cent. of clupanodonic acid. H. Okada (*ibid.*, 1909, 34, 62) found that the portion least soluble in a mixture of ether and alcohol contained oleic, stearic and iso-cetic acids. An attempt was made by M. Tsujimoto (*J.S.C.I.*, 1913, 32, 96) to separate the fatty acids by means of superheated steam, but with

only moderate success. J. A. B. Svendsen (*J.S.C.I.*, 1917, 36, 657) found that the fatty acids were in the following proportion: Myristic, 6; palmitic, 17, Bull's C_{16} acid, 12; stearin, 2; oleic, 7–8; isolinoleic, 6–7; gadoleic, 10; erucic, 16; clupanodonic, $C_{20}H_{30}O_2$, $C_{21}H_{32}O_3$ and $C_{22}H_{34}O_2$ together 7, and unidentified 10. C. Grimme (*ibid.*, 1921, 40, 267A) considers that the fatty acids present are approximately: saturated, 20; oleic, 20; linolic, 33; linolenic, 17; and clupanodonic, 9; whilst T. Lexow (*ibid.*, page 438A) considers that the presence of myristic, palmitic, zoomaric, stearic, oleic, clupanodonic, gadoleic and erucic acids is well established, whilst acids of the formulæ $C_{20}H_{30}O_2$ and $C_{22}H_{34}O_2$ with hydroxylated acids are also present; the oil from salted herrings contains in addition lactones, lipoids and soaps. An account of the products obtained by the dry distillation of the sodium salts of these fatty acids is given by Hirose and Yamada (*ibid.*, 1923, 43, 276A).

The methods of obtaining the oil and of refining are usually of quite a simple nature along the lines of those described under menhaden oil on page 436. The characteristics of the oil which are similar for the European and Japanese varieties are given below:

Characteristics of Herring Oil

Specific gravity	0·918–0·925
Acid value	2·0–42·0
Saponification value	[1] 186–191
Iodine value	[2] 130–140
n^{40}	1·4707
Melting-point of fatty acids °C.	about 30
Insoluble bromide value	13–22
Unsaponifiable matter	[3] 0·9–2·0

[1] Bull (*Chem. Zeit.*, 1899, 23, 1043) found 179–193·7 for *C. harengus*. [2] Tsujimoto found 103–123 for *C. pallasi*. [3] Bull reports figures as high as 10·7 per cent.

The characteristics of blown herring oils have been studied by Procter and Holmes (*J.S.C.I.*, 1905, 24, 1287), who also give characteristics of the untreated oils. Cf. also A. Lusskin (*ibid.*, 1912, 31, 935) and J. Lund (*ibid.*, 1914, 33, 756).

M. Tsujimoto (*ibid.*, 1915, 34, 1259) has examined samples of fish oil stearine and oleine, and soap stock fatty acids said to be obtained mainly by distillation from the fatty acids of Japanese herring oil with the following results:

Table CCL.—Tsujimoto's Analysis of Fatty Acids from Herring Oil

	Stearine.	Oleine.	Soap Stock Fatty Acids.	
			1.	2.
M.Pt °C	53·5	..	39·5–40	37·5–38·5
Solidifying-point °C. (titre test)	52	..	..	..
Sp. gr. 15°/4°	..	0·9009	..	..
Neutralisation value	213·65	169·67	201·90	196·65
Saponification value	214·56	191·05	210·30	202·98
Iodine value (Wijs)	17·38	63·38	38·41	42·70
Unsaponifiable matter	..	4·78%	1·83%	2·87%

Lesser-known Fish Oils.—It is not necessary to consider these in detail, but the following table due to J. F. Liverseege (*Analyst*, 1904, 29, 210) will give useful information.

TABLE CCLI.—ANALYSIS OF LESSER-KNOWN FISH OILS (LIVERSEEGE)

	Seal.	[2] Shark.	Dugong.	Haddock.	Menhaden.	Whale.	Brusmer.	Hoi.	Li
S.G. 15·5° . .	0·925	0·962	0·919	0·934	0·931	0·917	0·923	0·919	0·9
n_D^{40}	1·4685	1·4770	1·4607	1·4750	1·4732	1·4633	1·4700	1·4689	1·4
Rotation (200 mm. tube)	0	−0·5	−0·1	−0·5	−0·4	−1·0	−0·5	−4·0	−
Hübl. Iodine per cent. . . .	132	142	69	179	174	94	138	124	13
KHO required per cent. for free acid . .	0·5	2·2	0·5	0·6	0·5	0·4	0·1	0·1	
KHO total per cent. . . .	19·4	6·0	20·2	19·3	19·3	18·8	18·3	16·9	1
[1] Valenta test (°C.)	88	35	86	73	78	100	108	113	10
Unsaponifiable matter per cent.	1·0	84·0	0·9	1·0	0·6	1·0	..	..	

[1] Butter = 65°. [2] Cf. A. Rogers, *J.S.C.I.*, 1926, 45, B19.

The following numbers due to Tsujimoto (*J.S.C.I.*, 1913, 32, 434) are also useful for reference purposes:

TABLE CCLII.—VALUES FOR LESSER-KNOWN FISH OILS (TSUJIMOTO)

Oil.	Sp. Gr. 15°.	Acid Value.	Sap. Value.	Iodine Value (Wijs).	Refrac. Index at 20°.	M.Pt. of Fatty Acids.	Hydroxy Acids.
						C.	Per cent.
Sea-lion oil . .	0·9278	0·58	189·80	156·37	1·4783	29·5	..
Bonito oil (1) .	0·9339	15·80	184·69	208·92	1·4843	34·5	0·63
,, ,, (2) .	0·9293	4·36	182·64	189·45	1·4820	32·0	0·49
Tunny-fish oil .	0·9327	20·85	185·32	198·90	1·4837	31·0	0·62
Mackerel-pike oil	0·9223	14·47	184·74	139·81	1·4760	26·96	0·26
Mackerel oil .	0·9301	1·72	191·63	167·43	1·4811	..	..
Akajei oil . .	0·9268	1·72	186·98	161·95	1·4784	32·5	..
Suketo-tara oil .	0·9279	1·18	187·87	169·58	1·4798	31·3	..
Eel oil . . .	0·9218	0·0	200·60	107·42	1·4712	36·0	..
Snapping-turtle oil	0·9229	0·45	195·65	121·09	1·4737	32·8	..

The preparation of artificial petroleum from fish oil is dealt with by Kobayashi and Yamaguchi (*J.S.C.I.*, 1922, 41, 242A) and the action of the silent electric discharge on fish oils by L. Hock (*ibid.*, 1923, 42, 508A).

Liver Oils

Cod-liver Oil

Although many liver oils have been examined from time to time the only one that is of commercial importance is that of the cod, of which enormous quantities are produced. At one time the only source of medicinal oil was in Norway, but of late years the Newfoundland industry has made great strides and the product is now the equal in most respects of the Norwegian variety.

Cod-liver oil is obtained from the liver of the common cod fish, *Gadus morrhua*, which frequents the northern coasts in enormous quantities at various times of the year. At the Lofoten Islands in Norway, for instance, the fishing season lasts from February to April. In the first instance the cod livers were simply a by-product of the cod-fishing industry and the oil was obtained after the livers had become rancid, consequently the product was very inferior. When the valuable medicinal properties of the oil were recognised the methods of preparation were considerably altered and with improved methods of transport it is now possible to obtain an oil of good flavour without any drastic methods of refinement which are likely to prejudice its use for medicinal purposes.

Preparation.—The modern methods for its preparation have been described at length in a series of papers by Drummond and Zilva. One describing the Norwegian methods (*J.S.C.I.*, 1922, 41, 280T) has been abstracted in the following way (*Analyst*, 1922, 47, 445) :

" This paper is based upon a visit made by the authors to the chief Norwegian centres of the cod-liver oil industry, and subsequent examination of the samples then collected. The oil is obtained from the livers by three chief methods : (*a*) The old-fashioned rotting process, in which the livers are stored in wooden vats for long periods, when the oil separates and collects upon the surface; (*b*) heating in steam-jacketed pans; and (*c*) heating by direct steam, in which process live steam is blown into a mass of livers, and the oil is skimmed off after separating. The small amount of crude oil produced by the first process is rarely used for medicinal purposes, but that obtained by the other methods is refined by freezing and the removal of ' stearine,' this being occasionally followed by treatment with an adsorbent for the removal of pigment. Whichever method of preparation and refining is adopted, the vitamin A content is practically unaffected, excepting during the bleaching of dark-coloured oils, which is however rarely done. The variations observed in the vitamin content are believed to depend upon the changes in diet or the physiological condition of the fish at different seasons. The stearine removed during refining was found to possess a high vitamin content, but is generally used for technical purposes."

In a later paper (*J.S.C.I.*, 1923, 42, 185T) the same authors give an account of the Newfoundland industry which is based on their visit to the fishing-grounds. The results of their investigations have been stated as follows (*Analyst*, 1923, 48, 337) :

" The oil is obtained under hygienic conditions, and the second fraction which is allowed to be used only for industrial purposes, possesses a vitamin potency almost equal to that of the first fraction. Oils obtained in 1919, 1920, and 1921 showed no variation in vitamin content. The method adopted for refining the oil consists in chilling and allowing the stearin to settle out. This stearin, comprising from 3 to 5 per cent. of the oil, although used for technical purposes has a vitamin potency considerably higher than that of

butter. For this reason the unrefined oil contains a larger proportion of vitamin than the same material after refining, and the former would probably be of greater medicinal value, and could be employed in the form of emulsions. Owing to their greater purity the Newfoundland oils are superior to those produced in Norway, although the opinion of the medical profession is in favour of Lofoten oils. The imports of Norwegian oils into this country are approximately five times the quantity of those from Newfoundland."

The excellence of the Newfoundland produce is assured by the fact that in 1916 by an act of the Newfoundland Legislature all the cod-liver oil production of the colony was put under the control of the Ministry of Marine and Fisheries. Every cod-liver oil manufacturer is required to hold a licence issued by this Government Department. Rules are laid down for the preparation of the oil. Government inspectors visit the factories to see that the regulations are complied with and also to instruct the manufacturers in the approved method of manufacture. These inspectors act in conjunction with the Government Analyst. A certificate of inspection must be produced by the exporter to the Customs Officer before shipping his goods.

The direct steam process is almost entirely used now in Newfoundland. There are a few jacketed plants still in operation, but the Ministry of Marine and Fisheries will not allow these to be renewed, so that in a few years nothing but the direct steam process will be operating. The person in charge of the factory must see that the livers are fresh, all brown and poor livers being discarded. The gall-bladder must not adhere to any of the livers. Previous to steaming the livers are washed in a tub of clean fresh water; the steam-pan too, must be in a perfectly clean condition before commencing the operation. The steam is passed into the livers until a white scum floats. It takes usually about thirty minutes to arrive at this condition. After turning the steam off, the brew is allowed to settle for about five minutes. The oil is then decanted and strained through flannel, calico, or moleskin into a cooling tank of galvanised iron where it remains until the following day. It is then dipped and strained through a double calico bag. The strained oil is received in a tin chute, which conveys it to the cask, before entering which it is filtered once more through a funnel covered with cheese cloth. In washing the pans, the utensils, and cloths, only soap and water are employed; the use of soda is not allowed.

Composition.—The composition of cod-liver oil has been studied by various workers. W. Fahrion (*J.S.C.I.*, 1893, 12, 935) considers that jecoric acid may be present, although he could not identify it with certainty, and suggests the presence of an acid of the formula $C_{17}H_{32}O_2$. Heyerdahl describes experiments to show that palmitic, jecoleic and therapic acids are present, whilst oleic and hydroxylated acids are absent.

H. Bull has contributed considerably to our knowledge of the composition of cod-liver oil. In his later paper (*Analyst*, 1907, 32, 25, cf. *Chem. Zeit.*, 1899, 23, 996) he uses the method of alcoholysis and considers that he has proved the presence of myristic, palmitic, stearic, oleic and erucic acid together with acids of the formulæ $C_{16}H_{30}O_2$ and $C_{20}H_{38}O_2$. The opinion is expressed that Heyerdahl's jecoleic acid could not have been present to any great extent.

M. Tsujimoto (*J.S.C.I.*, 1913, 32, 433) found that the fatty acids of two commercial samples yielded 34·4 and 36·2 per cent. of octobromide respectively which approximated closely to the composition of therapic octobromide. J. J. Cerdeiras (*ibid.*, 1916, 35, 477) states that he has isolated the glyceryl ester of tetra-chlorotetraiodotherapic acid $C_3H_5(C_{17}H_{23}O_2Cl_4I_4)_3$. Berghausen and Steinkoenig (*ibid.*, 1922, 41, 32A) state that, by extracting cod-

liver oil with acidified alcohol and purifying the yellow oil obtained, they prepared morrhuic acid, $C_9H_{13}NO_3$, which is probably hydroxydihydropyridine-butyric acid. (Cf. *ibid.*, 1910, 29, 639; 1911, 30, 1169.)

The vitamin A content of the oil has been studied by various workers: Takahashi and Kawakami (*ibid.*, 1923, 42, 904A.), Hattori and Obata (*ibid.*, page 987A.) A. D. Holmes (*Analyst*, 1924, 49, 240; 1925, 50, 80). Hess and Weinstock (*J.S.C.I.*, 1925, 44, B609). Dubin and Funk (*ibid.*, p. B897).

Properties and Uses.—The great importance of cod-liver oil lies in its value as a curative agent in those diseases which are caused either directly or indirectly by malnutrition, the chief one being tuberculosis. For a long time it was considered that the therapeutic powers of the oil were due either to its ease of digestion (although why this should be so is a little difficult to imagine) or to the presence of small quantities of halogens, particularly of iodine. It was generally recognised that although these might be reasons they were scarcely explanations, and it would appear that the more recent discovery of comparatively large amounts of vitamin A is a much more likely cause; this is discussed in outline on page 477. It follows that, if this be the case, the testing of cod-liver oil should be by biological methods, in additions to chemical methods; such are, however, outside the scope of the present work.

Some attention has been directed to the use of this oil for the feeding of farm stock by J. C. Drummond and his co-workers (*Analyst*, 1923, 48, 337, 339).

Attempts have been made to remove the disagreeable odour and taste from the oil with the idea of using it as a substitute for cotton-seed oil and neutral lard. Encouraging results have been reported (*J.O.F.I.*, 1924, 1, 55).

The sulphuric acid test with liver oil has already been fully described on page 77. P. J. de Kadt (*J.S.C.I.*, 1920, 39, 550A) states that oils which have been treated with bleaching agents such as fuller's earth or animal charcoal no longer give the reaction, as the substances which cause this are absorbed by the agent.

Radcliffe and Palmer (*ibid.*, 1915, 34, 643) have examined the fatty acids of cod-liver oil after sulphonating the latter with 35 grms. of concentrated sulphuric acid for 100 grms. of oil at a temperature of 25° or less. Their results are given in the following table:

	Fatty Acids from Original Oil.	Fatty Acids from Sulphonated Oil.
Solidifying-point (titre test) °C. .	22·8	25·7
Neutralisation value	194	183
Mean molecular weight . . .	289·4	308·6
Iodine value	178	114·4
Yield of hexabromides	42 per cent.	11 per cent.

Examination.—The chief difficulty in the examination of cod-liver oil for the presence of adulterants lies in detecting the presence of other fish oils. On account of the fact that medicinal oils must be of good colour and flavour this difficulty is to some extent lessened, but, nevertheless, adulteration of this nature has taken place in the past. A method for the detection of menhaden oil has been proposed by A. Hoppenstedt which is described on page 437, other fish oils such as shark-liver oils may be detected by an

increase in the amount of unsaponifiable matter present which, in the best oils, does not exceed 1·5 per cent. The iodine value is useful. The refractive index has been shown by various workers to vary only within fairly narrow limits, whilst possible adulterants give, frequently, widely different figures. (J. F. Liverseege, *Analyst*, 1904, 29, 210.)

The determination of the insoluble bromide value should be useful as many of the likely adulterants yield results which are considerably lower than those given by cod-liver oil.

Liverseege (*loc. cit.*) showed that the Valenta test was a useful one in the examination of cod-liver oil as, whilst various samples gave results almost identical many of the likely adulterants gave widely different results. This suggestion was followed up by E. Louise (*Analyst*, 1907, 32, 365; 1910, 35, 322; 1911, 36, 275) who suggests plotting the miscibility curves of the oil with acetone. For further particulars of this method which may give useful results in different cases, reference should be made to the original papers and to the subject of miscibility curves in general on page 94.

Many of the characteristics given in the older papers on cod-liver oil were obtained on rancid samples and are of little value to-day. Those obtained from medicinal oil are reasonably constant as the following figures taken from the *Annual Reports* of Messrs Southall Bros. and Barclay (E. W. Mann) extending over many years amply testify:

Iodine value	162–168 (154·8–172·5)
n^{40}	1·4701–1·4717
Unsaponifiable matter	0·69–1·47

In the table of characteristics of the oil given below three series of figures are therefore given.

TABLE CCLIII.—CHARACTERISTICS OF COD-LIVER OIL

	Medicinal Oil.		Commercial Qualities.
	Average Values.	Usual Variations.	
Specific gravity 15°/15°	0·926–0·927	0·925–0·929	0·922–0·930
Saponification value	183–188	182–188	180–190
Iodine value	160–170	155–181	140–190
Reichert value	0·2	0·1–0·6	0·3–2·5
n^{40}	1·4705–1·4715	1·4700–1·4730	1·4690–1·4740
Unsaponifiable matter	0·8–1·4	0·7–1·5	0·7–3·0
Acid value	0–0·4	0–28	1–40 (and higher)

Characteristics of the Fatty Acids :

Titre °C.	14–25
Iodine value	164–176

It should be remembered that medicinal oils are always chilled and filtered which thus removes a portion of the stearine; the values of the oil are, of course, considerably altered by this process. (Cf. J. Lund, *J.S.C.I.*, 1914, 33, 756 and H. Thaysen, *ibid.*, page 322.)

The *B.P.* has the following paragraph for the requirements of the medicinal oil:

"Cod-liver oil is the oil expressed from the fresh liver of the cod, *Gadus morrhua*, Linn., at a temperature not exceeding 85°, and from which solid fat has been separated by filtration at about −5°.

"*Characters and Tests.*—Pale-yellow. Slight, fishlike, but not rancid odour; taste bland, fishlike. Specific gravity 0·920 to 0·930; saponification value 179 to 192; iodine value 155 to 173; acid value not more than 2·5; refractive index at 40°, 1·4704 to 1·4745; unsaponifiable matter not more than 1·5 per cent. When exposed for three hours to a temperature of 0°, no solid fat separates."

The monograph in the *United States Pharmacopœia* is as follows:

"A fixed oil obtained from the fresh livers of *Gadus morrhua*, Linn., and of other species of *Gadus* (Fam. *Gadiœ*). Preserve it in a cool place, in well-closed containers, which have been thoroughly dried before filling.

"Cod-liver oil is a pale-yellow, thin, oily, liquid, having a peculiar, slightly fishy, but not rancid odour, and a fishy taste.

"It is slightly soluble in alcohol; soluble in ether, chloroform, carbon disulphide, or ethyl acetate.

"Specific gravity: 0·918 to 0·922 at 25 C.

"A solution of 1 drop of the oil in 1 mil of chloroform when shaken with 1 drop of sulphuric acid acquires a violet-red tint, gradually changing to reddish-brown.

"Allow 2 or 3 drops of fuming nitric acid (specific gravity about 1·44) to flow alongside of 10 or 15 drops of the oil contained in a watch glass; a reddish or purplish colour is produced at the zone of contact. On stirring the mixture with a glass rod, this colour becomes bright rose-red (distinction from seal oil, which shows no change in colour, and from other fish oils, which become blue).

"Cod-liver oil is only slightly acid to litmus paper which has been previously moistened with alcohol (free fatty acids). Saponification value: not less than 180, not more than 190. Iodine value, not less than 140, not more than 180."

This monograph has been rather severely, and not altogether unjustly, criticised by H. C. Fuller (*The Chemistry and Analysis of Drugs and Medicines*. New York and London 1920) in the following words:

"The figures given in the 9th Revision of the *U.S.P.* as applying to a cod-liver oil of standard purity are nearly all incorrect, and the test for the limit of free fatty acids is vague and of no value. Oils of high purity will often contain nearly 1 per cent. of free acid. The figures and the colour tests together are not limited to cod-liver oil, but will apply equally well to carefully refined oils from other fish livers; though it should be stated that in this investigation the oils from the livers of American cod and other American fish lose their original character and become unfit for medicinal use after three to four years."

Blubber Oils

Seal Oil

Seal oil is obtained from the blubber of various species of seal. Various methods have been used for the preparation of the oil-giving products of varying degrees of purity. The more modern methods follow closely those obtaining in the case of whale oil, which are described below on page 448.

The composition of seal oil has not been worked out at all fully. Bauer and Neth (*J.S.C.I.*, 1924, 43, B183) working on an old sample found that the fatty acids consisted of palmitic acid, physetoleic acid (hexadecylenic) and small quantities of clupanodonic acid. Similar results have been obtained by M. Tsujimoto. This work, obviously, is not of a final character and further investigation is desirable. (Cf. A. Wingard, *J.S.C.I.*, 1911, 30, 1022.)

Figures for the characteristics of seal oil have been published by various workers as J. F. Liverseege (*Analyst*, 1904, 29, 210), Schneider and Blumenfeld (*ibid.*, 1906, 31, 78), A. P. Lidoff (*ibid.*, 1911, 36, 21), J. Lund (*J.S.C.I.*, 1914, 33, 756), M. Tsujimoto (*ibid.*, 1916, 35, 1069). These and other figures are summarised in the following table:

TABLE CCLIV.—CHARACTERISTICS OF SEAL OIL

Specific gravity 15°/15°	0·924–0·926
Iodine value	130–150 (193)*
Saponification value	185–195
n^{40}	1·4680–1·4700
Unsaponifiable matter	0·4–1·5
Acid value	0·0–40·0

WHALE OIL

Whale oil is extracted from the blubber of various species of whale (*Balœna*) which occur both in northern and southern waters. The whaling industry has suffered many vicissitudes at various stages in its industry (cf. the interesting account of W. Mansbridge, *J.S.C.I.*, 1917, 36, 362) and at one period became almost extinct, but the use of more modern weapons and apparatus has enabled the industry to carry on.

Preparation.—The older methods by which the blubber was allowed to rot naturally resulted in inferior oils, but in the more modern methods a "floating factory" is used to enable the oil to be prepared immediately on the successful completion of the chase. The following is the account of the methods used, given by Mansbridge (*loc. cit.*):

"The usual method of working such distant waters as the South Pacific and South Atlantic is for the floating factory to sail with supplies for the land stations towards the end of summer. This cargo consists of coal, provisions, building material, machinery and general stores, including empty barrels, the coal being carried in the oil tanks. After discharging at say South Georgia, the tanks are cleaned out ready for oil and the factory ship, accompanied by its fleet of fishing vessels, departs for the cruising ground which may be at the edge of the Antarctic ice. The actual pursuit and killing of the whale is done by small steamers of about 120 tons; the gun is mounted in the bows and naturally the skill of the gunner is an important matter. On sighting a whale the vessel is allowed to drift near enough to the animal as it rises to blow within range, the harpoon is fired into it, out goes the thick cable, and if the shot has been a good one the whale is soon alongside, wound in by the steam winch and inflated through a hollow lance to make it float easily; as many as four may be secured in this way and taken to the floating factory on to the land station for disposal. The bomb harpoon, frequently employed, has an explosive head fired by a time fuse and if well planted in the whale death quickly ensues.

"The floating factory is often an old liner filled with tanks for the reception of the oil; even the ballast tanks are utilised for the same purpose; some have a few large tanks built into them, others have as many as 80 or 90 small

* Schneider and Blumenfeld.

tanks; barrels from the land stations are carried in the 'tween decks, and the upper deck amidships is occupied by the ' cooker tanks,' as the digesters in which the blubber is rendered or ' tried out ' are called. The cooker tanks are arranged in pairs; they are strong iron vessels capable of standing a pressure of 100 lb. per sq. inch, with a wide manhole at the top for charging and one near the bottom for discharging the exhausted blubber, and perhaps one pair will be fitted with extra large openings 4 ft. diam. for the reception of bones, such as ribs and vertebræ; curved iron plates are used to provide a free passage for the steam through the mass of blubber.

" Arrived alongside, the operation of ' flensing,' which consists in stripping the blubber from the dead whale, is at once commenced; huge pieces are hoisted on board, put through the chopping machine, taken up by an elevator and dropped into the cooker, steam is turned on and after a sufficient period, generally six to eight hours, the oil is run off through a system of separating tanks to get rid of the free water, then into the store tanks in the lower part of the ship.

" The process of cooking is of very great importance; upon the skill and care with which it is conducted depends whether the oil will reach the market in good condition or much depreciated in value, hence the cook shares with the gunner the honours of a successful voyage. As the largest number of cargoes arrive during March to July it follows that a large part of the season's oil is upwards of six months old, and it may even be eighteen months old when marketed, so that unless properly cooked it will keep badly and in consequence fetch a lower price when landed. The ambition of most cooks is to produce a very pale oil; this is not an easy matter even from very fresh whales if the oil is well cooked, but unfortunately quite simple if undercooked. I have been informed that cold pressing with hydraulic presses has been tried with the object of obtaining a very pale-coloured oil, but, as might be expected, the oil quickly became rancid and bad in other ways and the idea was soon abandoned. The best cook is one who is able to get the largest yield of pale oil with the best keeping qualities; this also best fills the requirements of both parties, the producer of the oil and the merchant who buys it from him. It has always been my advice to the captains of floating factories to make a well-cooked oil that will grade ' No. 1 ' and let the superfine colour go, because if stored it always depreciates and falls to No. 1 standard or lower; they generally see the force of this, particularly as nowadays they do not get a premium for extra pale oil." (Cf. H. T. Offerdahl-Larvik, *ibid.*, 1914, 33, 32.)

Whale oil is marketed according to grade, the grade numbers varying from 0 to 4 with 0 as the best article. The grading depends largely upon the colour on which point the following further remarks of Mansbridge are of value.

" The accepted grades are known as No. 0, No. 1, No. 2, No. 3 and No. 4. No. 0 and No. 1 are now generally classed together, the former being regarded as a superfine No. 1; the colour varies from pale straw-colour to fine pale-yellow. No. 2 is amber-yellow and No. 3 pale-brown, while anything too dark to be classed as No. 3 is regarded as No. 4, unless it is very bad coloured when it is referred to as ' dark whale oil.' "

In order to examine crude whale oil in the tintometer it is necessary to warm it slightly in order to melt the stearine; a temperature of 75°–80° F. is sufficient for the purpose. The oil as delivered by the ship, always contains moisture which should not exceed 0·5 per cent. The sample must not be heated sufficiently to drive off water, and besides, this would probably darken the oil to some extent, neither must filtration be resorted to as thereby colour might be removed. Considerable care is therefore needed to obtain

accurate results, but a little practice will soon overcome any difficulty in the preparation of the sample.

The colours in Lovibond's neutral tint series are as follows:

TABLE CCLV.—LOVIBOND'S NEUTRAL TINT SERIES

	Red.	Yellow.	Blue.
No. 0	1·8	5·6	0·8
No. 1	5·0	20·0	2·0
No. 2	7·0	30·0	1·9
No. 3	26·0	80·0	1·5
No. 4	Not required.		

All in one-inch standard cell.

For an account of the quality of glycerol obtainable from whale oil see A. H. Salway (*ibid.*, 1918, 37, 123T) and Cocks and Salway (*ibid.*, page 126T).

Composition.—The composition of whale oil has been studied by several observers; H. Bull (*J.S.C.I.*, 1895, 14, 130) was one of the earliest. M. Tsujimoto (*Analyst*, 1906, 31, 344) discovered clupanodonic acid as a constituent. The most complete investigation so far attempted is that of Milligan, Knuth and Richardson (*ibid.*, 1924, 49, 149) who, by a combination of the Twitchell modification of the lead-salt-ether method and of the method of alcoholysis found the following approximate composition of the fatty acids; Myristic, 4·5; palmitic, 11·5; palmitoleic, 17·0; stearic, 2·5; oleic, 36·5; C_{20} unsaturated, 16; C_{22} unsaturated, 10; C_{24} unsaturated, 1·5. Like so many of the other fish oils, and indeed of all oils, much further work is desirable along these lines as a large proportion of the constituents is still obscure. An extensive investigation has recently been undertaken by E. F. Armstrong and Hilditch (*J.S.C.I.*, 1925, 44, 180T) into the constitution of the unsaturated acids of whale oil.

Y. Toyama (*J.S.C.I.*, 1924, 43, B1019) has examined the fatty acids of the oil of the hump-backed whale and the finner whale with the following results:

TABLE CCLVI.—EXAMINATION OF WHALE OIL (TOMANA)

	Hump-backed.	Finner.
Saturated acids	10 per cent.	25 per cent.
Highly unsaturated acids	15 „ „	15 „ „
Saturated acid present	Palmitic, Myristic, Arachidic (?), Behenic (?)	Palmitic, Myristic } Majority; Stearic, Arachidic, Behenic
Simple unsaturated acids	Oleic, $C_{16}H_{30}O_2$, Iso-erucic acid, $C_{20}H_{38}O_2$, $C_{14}H_{26}O_2$ (?)	Oleic, $C_{16}H_{30}O_2$ } Chief; $C_{20}H_{38}O_2$, $C_{22}H_{42}O_2$, $C_{14}H_{26}O_2$ (?)
More unsaturated acids	$C_{18}H_{28}O_2$, $C_{18}H_{30}O_2$, $C_{18}H_{32}O_2$, $C_{20}H_{30}O_2$, $C_{20}H_{32}O_2$, $C_{22}H_{34}O_2$ *, $C_{22}H_{36}O_2$	Similar to hump-backed but rather larger quantities.

* Probably clupanodonic acid.

Myddleton and Barry (*Fats : Natural and Synthetic*, 1924, page 110) give as the composition of Newfoundland whale oil, myristic 9, palmitic 10, stearic 3, palmitoleic 18, oleic 35, linoleic 9, and arachidonic 16, whilst South Sea whale oil is said to contain myristic 8, palmitic 12, palmitoleic 17, oleic 25, linoleic 20, $C_{22}H_{36}O_2$ 18.

Hardened whale oil has been examined by B. Svendsen (*J.S.C.I.*, 1917, 36, 603). A sample with acid value 1·5, saponification value 195·7, iodine value 59·8, and which yielded no insoluble bromide consisted of 10·8 per cent. of myristic acid, 17·9 per cent. of palmitic acid, 10·6 per cent. of Bull's C_{16} acid, 10·8 per cent. stearic acid, 27·7 per cent. of oleic acid, 3·4 per cent. of arachidic acid, 8 per cent. of a solid acid, $C_{22}H_{36}O_2$, 2·5 per cent. of behenic acid and 8·8 per cent. of a solid acid, $C_{22}H_{40}O_2$.

Buttenberg and Angerhausen (*ibid.*, 1920, 39, 121A) state that the unsaponifiable matter of whale oil after removal of the cholesterol is distinctly optically active, $[\alpha]_D = 2°$, in contradistinction to that from other animal fats. They further state that whale oil yields, when crystallised from acetone, a larger quantity of insoluble glycerides than do animal fats.

TABLE CCLVII.—CHARACTERISTICS OF WHALE OIL

Specific gravity 15°/15°	0·920–0·927
Saponification value	180–197
Iodine value	105–135
n^{40}	1·4630–1·4710
Titre of fatty acids °C.	22–25
Insoluble bromide value	25–30
Acid value	Upwards of 1

An examination of the oil of various Pacific Ocean whales has been made by W. M. Doherty (*Analyst*, 1923, 48, 495) with the following results :

TABLE CCLVIII.—ANALYSIS OF WHALE OILS (DOHERTY)

Source of Oil.	S.G. at 15·5°.	R.I. at 40°.	Sap. Value.	Acid Value.	Iodine Value.
Blubber of Sei whale	0·9182	1·4651	195	0·75	99·6
Bones „ „ „	0·9186	1·4621	197	1·25	86·4
Blubber of hump-back, 1	0·9232	1·4661	194·5	5·80	108
„ „ „ 2	0·9212	1·4670	192	1·00	119
Tongue „ „	0·9212	1·4640	199	2·2	105
Tongue of blue whale	0·9197	1·4626	194	0·87	95
Stearine from hump-back	0·9204	..	192	35·00	92
Oil and spermaceti from head cavities of sperm whale	0·8779	1·4542	145	12·7	66
Oil from blubber of sperm whale	0·8796	1·4578	127	3·0	89

The oil of the sperm whale, sperm oil, is sharply distinguished from other species by its high content of spermaceti and unsaponifiable matter; it is a liquid wax and not a fatty oil. Some characteristics of this oil are given in the following table but vary according to the amount of stearine (spermaceti which is chiefly cetyl palmitate) which has been allowed to remain, this in turn depending upon the temperatures at which the stearine has been separated.

TABLE CCLIX.—CHARACTERISTICS OF SPERM OIL

Specific gravity 15°/15°	0·878–0·883
Iodine value	80–90
Saponification value	125–140
n^{40}	1·4580–1·4620
Unsaponifiable matter	37–43

Spermaceti (the stearine of sperm oil) has specific gravity 0·950–0·960, saponification value 125–135, iodine value 3–4·5, M.Pt. about 50°.

Hydrogenated Whale Oil.—Characteristics have been published by various observers for the hydrogenated product of whale oil. A selection of these is given in the following table:

TABLE CCLX.—CHARACTERISTICS OF HYDROGENATED WHALE OIL

Observer.	M.Pt. °C.	Titre. °C.	M.Pt. Acids. °C.	Sap. Value.	Iodine Value.	n^{60}.
[1] E. Mellana	52·5	44	49	169·5	28·8	1·4517
[2] A. E. Sandelin	41·9	..	..	190·9	57·8	1·4504

[1] *J.S.C.I.*, 1914, 33, 701. [2] *Ibid.*, page 1097.

Dolphin and Porpoise Oils.—These oils are extremely interesting in that they contain large quantities of volatile acids so that their Reichert values are very high, figures of as much as 112 having been obtained. The oils from the jaw and from the body differ considerably in composition. It has been suggested that the volatile acid is valeric, but this stands in need of confirmation. The writer has attempted on many occasions to obtain authentic samples of this oil but always without success. E. André (*Analyst*, 1924, 49, 296) states that he has confirmed the presence of isovaleric (isopropyl acetic) acid. (Cf. Nakatogawa and Kobayashi, *J.S.C.I.*, 1922, 41, 556A.)

M. Tsujimoto (*ibid.*, 1913, 32, 434) has determined the following characteristics for dolphin oil (Cf. *ibid.*, 1923, 42, 276A.):

TABLE CCLXI.—CHARACTERISTICS OF DOLPHIN OIL (TSUJIMOTO)

	Oil from Head.	Oil from Body.		Refined Head Oil.
		Boiling Process.	Roasting Process.	
Specific gravity 15°/15°	0·9249	0·9286	0·9307	0·9259
Saponification value	279·78	217·22	230·35	277·70
Iodine value	24·48	125·25	114·35	25·67
Reichert-Meissl value	112·31	30·40	44·39	..
Refractive index at 20°	1·4524	1·4717	1·4695	1·4517
Butyro-refractometer	40·0	69·0	65·5	39·0
Acid value	2·30	11·90	3·97	0·26
Octobromides of fatty acids, per cent.	..	24·75	..	..

The following characteristics of porpoise body oil are given by Schneider and Blumenfeld (*Analyst*, 1906, 31, 78):

TABLE CCLXII.—CHARACTERISTICS OF PORPOISE BODY OIL (SCHNEIDER AND BLUMENFELD)

Specific gravity 15°/15°	0·933
Acid value	1·2
Saponification value	224·8
Iodine value	111·2
Reichert value	42·1
n^{40}	1·4621
Titre °C.	18°
Iodine value of acids	126·0

HYDROGENATED FISH OILS

Various types of tallow-like substances are now prepared by the hydrogenation of fish oils. Some of these have been described under the individual oils in the preceding section; the following additional information may be found of value. Two samples of such products examined by C. Grimme (*Analyst*, 1913, 38, 373) had the following characteristics.

TABLE CCLXIII.—SAMPLES OF HYDROGENATED FISH OILS (GRIMME)

Sp. Gr. at 15°.	M.Pt. °C.	Sol. Pt. °C.	n_D^{40}.	Acid Value.	Saponification Value.	Iodine Value (Wijs).
0·9271	47·2	34·9	1·4529	1·94	189·3	23·24
0·9200	38·5	31·6	1·4575	1·00	188·8	58·34

Grimme also studied the colour reactions of the hardened products and gives the following results:

TABLE CCLXIV.—COLOUR REACTIONS OF HARDENED FISH OILS (GRIMME)

	Hardened Oils.			
	Seal Oil.	Whale Oil.	Liver Oils.	Fish Oils.
Fuming nitric acid	Red-brown	Brown afterwards black-brown	Blood-red, then bluish-red to brown	Brown
Sulphuric acid (sp. gr. 1·65–1·70)	Red-yellow then brown-red	Brown, then black-brown	Violet to violet-black	Green then brown to black
Nitric and Sulphuric acids (1 : 1)	Red, then brown	Yellow, then red-brown	Yellowish-red, onion red, and finally red-brown	Yellow, green to brown

TABLE CCLXIV.—*continued*

	Hardened Oil.			
	Seal Oil.	Whale Oil.	Liver Oils.	Fish Oils.
Syrupy phosphoric acid	Brown	Red-brown	Red	Red-brown
Aqua-regia . . .	Pale-yellow mass	..	..	..
Sodium hydroxide	..	Red-brown	Red	Red-brown
Phosphomolybdic acid (1%) added to chloroform solution of fat	Blue ring at junction of liquids	..	..	..

In a later paper Grimme states (*ibid.*, page 433) that the intensity of the colourations decreased with the degree of hardening, but that in each case it was possible to detect the presence of a marine animal oil. In particular, the test with 1 c.c. of sulphuric acid and 1 drop of tincture of iodine gave a very characteristic violet-red colouration in every instance.

CHAPTER XXIX

MEDICINAL OILS

Castor Oil

Source.—Castor oil is obtained by expression from the seeds of the castor plant, *Ricinus communis*, L. This plant is found in nearly all tropical and sub-tropical countries, in many of which it grows in enormous quantities. Whilst the plant grows wild in various regions it is also cultivated, as in India from whence the bulk of the present day supplies are received, so that the increasing demands that are being made on castor oil are not likely to cause any permanent shortage of supplies. Care is necessary in cultivation on account of the rapid exhaustion of the soil by the crop. The cultivation and utilisation of the castor plant is considered at length in a paper in the *Bulletin of the Imperial Institute* (*Bull. Imp. Inst.*, 1911, 9, 17).

The tree varies in size from a small shrub to a small tree reaching twenty feet or so in height. These differences are due to the existence of several species and also to the effect of climate and methods of cultivation. The seeds themselves also show considerable differences, both of size and colour. The most important distinction commercially is that of size; the classes may be roughly divided into large seeds and small seeds—the latter are, of course, more suitable for export, on account of the smaller bulk occupied by a given weight; but the expression of the oil is being more and more carried out in the country of origin, on account of the comparative uselessness of the cake except as a fertiliser, so that the bulk is becoming of less importance.

The seeds which have usually a characteristic mottled appearance are about the size of small beans. They contain 20 per cent. of husk, free from oil, and 80 per cent. of kernel. The average oil content of the seeds is about 50 per cent., the usual variations being from about 46 to 52. For the production of oil the seeds are first decorticated by lightly crushing between rollers, the husks removed by means of a blast of air, and then expressed in the cold. The first expression gives the finest oil (a yield of 30 per cent. and over being usually obtained) the only grade suitable for medicinal purposes. The reason for this is that the seeds contain a poisonous substance, ricin, which is not removed by pressure in the cold. The cakes thus obtained are expressed a second and a third time after heating, further quantities of oil being obtained suitable for manufacturing processes. The cake obtained from the last pressing usually contains up to 8 per cent. of oil, which is recovered by extraction with carbon bisulphide after the cake has been ground to a meal.

The exhausted meal is poisonous and is, therefore, useless in its ordinary condition for cattle feeding. It contains, however, a large proportion of nitrogen which makes it a valuable fertiliser, and for this purpose it is used in enormous quantities both in India and by the market gardeners of Southern France and elsewhere. Efforts have been made to remove the poisonous substances from the meal (cf. *J.S.C.I.*, 1902, 21, 30; *J. Board of Agric.*, 1918, 24, 1444) and this would now seem to be possible, but there is a prejudice of long standing against its use which will take a long time to overcome.

A test for the detection of castor seeds * in other seeds has been proposed by Lander and Geake (*Analyst*, 1914, 39, 292) whilst a test for the detection of lupin seeds in castor seeds has been suggested by Muenk (*J.S.C.I.*, 1915, 34, 678).

The oil is usually refined by steaming, which results in the coagulation of albuminous matters which may be filtered off; other processes of deodorisation are sometimes used.

Composition.—Castor oil consists largely of the glyceride of ricinoleic acid. Hazura and Grussner (*J.S.C.I.*, 1888, 7, 681) state that oleic acid is not present, but they report the presence of an isoricinoleic acid, but this has not been confirmed by Haller (*Compt. Rend.*, 1907, 144, 462), who found only stearic acid, ricinoleic acid and hydroxystearic acid, the latter compound having previously been discovered by Juillard. As a result of a consideration of the relationship between the iodine value of the oil and the acetyl value, together with the iodine value of the liquid fatty acids, Lewkowitsch is of the opinion that a less saturated fatty acid than ricinoleic is present, but it has not yet been isolated. It must be allowed that the composition of castor oil is not yet definitely settled. Eibner and Munzing (*J.S.C.I.*, 1925, 44, B679) found ricinoleic acid, 80; oleic acid, 9; linoleic acid, 3; stearic and dihydroxystearic, 3 per cent.

Properties.—Castor oil is remarkable among the fatty oils in that it is freely soluble in absolute alcohol and only slightly soluble in petroleum ether and also on account of its high specific gravity, viscosity, optical rotation and acetyl value; each one of these is a characteristic property of the oil. It is quite colourless and transparent when pure, but frequently has a greenish tinge which varies in depth according to the purity of the oil. It has a characteristic flavour very unpleasant to some, whilst to others it is unobjectionable. The *B.P.* states "that it should be nearly colourless, or with a yellowish tinge, viscid, liable to solidify at low temperatures, slight odour; taste at first bland but afterwards acrid and unpleasant."

Castor oil does not dry. On standing exposed to the air its specific gravity is increased without much increase in the acid value or decrease in the iodine value. On blowing air through at an elevated temperature, say 150°, the specific gravity and refractive index are increased and the iodine value decreased. (See Procter and Holmes, *J.S.C.I.*, 1905, 24, 1287.)

Characteristics.—An average sample of castor oil may be considered to have characteristics which are included in the table below:

TABLE CCLXV.—AVERAGE SAMPLE OF CASTOR OIL

Specific gravity 15°	0·958–0·968
Saponification value	177–187
Iodine value	82–90
Optical activity in 200 mm. tube	7·6°–9·7° (usually 8°–9°)
Index of refraction 40°	1·4705–1·4720
Acetyl value	147–150
Acid value	0·2–8·0 †
Reichert value	0·2–2·3
Titre °C.	3
Iodine value of acids	86·5–88·5
Unsaponifiable matter	0·3–0·6 per cent.

* Cf. J. W. Leathes (*Analyst*, 1892, 17, 121).
† Best samples not more than 4·0.

R. O. Jones has shown (*J.S.C.I.*, 1917, 36, 359) that hydrolysis of castor oil goes to completion by either the autoclave or the Twitchell process. The apparent incompleteness as shown by the acid value is due to the formation of polyricinoleic acids by the condensation of the ricinoleic acid molecule. The action of nitric acid on castor oil has been dealt with by W. F. Reid (*J.S.C.I.*, 1899, 18, 972) and R. Brightman (*J.S.C.I.*, 1917, 36, 984). H. Pomeranz (*J.S.C.I.*, 1916, 35, 642) has studied the behaviour of the sodium soaps of sulphonated castor oil in hard water.

Deering and Redwood found that the oil gave in Redwood's viscometer at 100° an efflux time of 1160 to 1190 seconds. Oil from Egyptian seeds sometimes gives abnormally low viscosities (W. R. G. Atkins, *Analyst*, 1919, 44, 287). The oil is miscible in all proportions with glacial acetic acid and absolute alcohol whilst it is soluble in three volumes of industrial methylated spirits (64° O.P.) at 15°. Finkener (*J.S.C.I.*, 1887, 6, 148) uses this as the basis of a test.

Special Tests.—As stated above Finkener shakes 10 c.c. of the oil with 50 c.c. of alcohol of specific gravity 0·83 when, if the oil is pure, complete miscibility should result. Frabot (*Analyst*, 1918, 43, 40) modifies the test by making a solution of one volume of the oil in five volumes of 95 per cent. alcohol and cooling the mixture below −20°. In the case of pure oils, it is stated, the liquid remains clear while as little as 2 per cent. of arachis oil will give an opalescence at −5° and a turbidity at −9°.

N. J. Lane (*J.S.C.I.*, 1907, 26, 597) bases a method for the determination of other liquid oils in castor oil on the insolubility of lead ricinoleate in petroleum spirit, the method being carried out much in the same way as the separation of solid and liquid acids.

About 3 grms. of the oil are saponified with alcoholic potassium hydroxide solution, and the soap solution is almost neutralised with acetic acid, using phenolphthalein as indicator. The liquid is then poured into an Erlenmeyer flask already containing 200 c.c. of boiling water and 30 c.c. of 10 per cent. lead acetate solution. The mixture is boiled for six minutes and then cooled by rotating the flask under a stream of cold water, the lead soap adhering to the sides of the flask. The aqueous solution is poured off or filtered, the lead soap is melted, cooled, and any remaining water drained away. The lead soap in the flask is then boiled out repeatedly with petroleum spirit, using about 225 c.c. in all, and the extracts and some insoluble lead soaps are collected in a 500 c.c. measure. The petroleum solution is diluted with more of the solvent, boiled for one minute, cooled, and made up to volume, and allowed to stand overnight, so that the insoluble lead ricinoleate may settle out. A known volume of the clear solution is drawn off, the solvent is evaporated until the residue measures about 75 c.c., and the latter then decomposed by the addition of 10 c.c. of 10 per cent. acetic acid. After washing the solution of the fatty acids in the petroleum spirit with water until free from water-soluble acidity, the mixture is distilled in order to remove most of the petroleum spirit; 50 c.c. of alcohol are added, and the solution is titrated with N/10 sodium hydroxide, the result being calculated into oleic acid.

Under these conditions castor oil gives practically no oleic acid so that a direct determination of the oleic acid in the adulterant is thus possible. Lane states that the percentage quantity of oleic acid found, divided by 80, gives the oils other than castor oil, this oil being then found by difference. The factor 80 is taken, since most of the oils used in the above materials are vegetable oils containing about 80 per cent. of liquid acids.

Frabot further suggests the shaking of 20 c.c. of the sample with 80 c.c.

of petroleum ether (boiling between 35° and 70°) in a stoppered graduated cylinder and allowing the liquids to separate. In the case of pure castor oil, he states, the increase in the volume of the oily layer, due to solution of the petroleum spirit, will be 11 or 12 c.c., but in the presence of foreign oils it will be greater, and the amount of increase affords a rapid criterion of the purification of the oil. After complete separation 50 c.c. of the petroleum spirit layer are evaporated and the residue weighed. Under these conditions twelve samples of pure castor oil yielded from 8·35 to 9·85 per cent. residue, the average being 8·52 per cent. By deducting the average figure from the amount of residue obtained from a mixture it is possible to estimate the amount of foreign oil present. This method is criticised by Chercheffsky (*Analyst*, 1918, 43, 218) but Frabot (*Analyst*, 1918, 43, 326), whilst admitting that the solvent power of petroleum ether varies with its origin, maintains that the process is accurate if a control test with pure castor oil is run at the same time (cf. Frabot, *J.S.C.I.*, 1918, 37, 98A). The reason for the variability in the solvent power of petroleum ether has been shown by W. R. G. Atkins (*J.S.C.I.*, 1920, 39, 521A) to be due to variations in the proportion of aromatic and naphthenic compounds as these latter increase the solubility of castor oil in the liquid.

Dealing with the petroleum ether test the *B.P.* states that 10 millilitres shaken with 7 millilitres of petroleum spirit in a stoppered glass cylinder form a clear mixture at 15·5°; on shaking with a further addition of 3 millilitres of petroleum spirit a turbid mixture is formed, which becomes clear when maintained for five minutes at 21°, but again becomes turbid when the temperature falls below 18° (absence of other fixed oils).

H. B. Stocks (*Analyst*, 1923, 48, 590) bases a new method of examination upon the fact that castor oil soaps exhibit very little dissociation in water as compared with those of other oils. The method consists in saponifying 5 grms. of the oil by means of 40 c.c. of N/2 alcoholic potash, neutralising the resulting liquid with N/1 hydrochloric acid and evaporating to dryness. The soap is dissolved in water and the solution diluted to 100 c.c. and 10 c.c. of this solution is poured into 250 c.c. of distilled water and the mixture titrated with N/10 hydrochloric acid to phenolphthalein. Under these conditions Stocks found that castor oil required 0·6–1·3 c.c., whilst other oils required quantities as below:

Arachis oil . .	9·3–9·5	Palm oil . . .	8·2–8·6
Olive oil . . .	8·2–8·5	Lard	9·2–9·4
Linseed oil . .	5·5–5·6	Tallow . . .	8·7–8·8
Rape oil . . .	7·7–8·0	Butter fat . .	7·4–7·9
Cotton-seed . .	7·3–7·4	Coconut oil . .	4·4–4·6
Palm-nut oil . .	5·2–5·3	Rosin	8·5

This method is interesting, but, at any rate until it has been given extended trial, it is not likely to supersede the more direct tests usually employed —it may be useful, however, in doubtful cases.

Detection of Adulteration.—The addition of any other oil to castor oil will lower the acetyl value or the optical activity (usually both) and will interfere with the solubility in alcohol and petroleum ether. Rosin oil has been used as an adulterant in the past but is readily detected by the amount of unsaponifiable matter present. For routine purposes it will usually only be necessary to take the specific gravity and the optical rotation and to test the solubility of the oil in alcohol and perform the B.P. petroleum ether test described above. Should any of these cause any suspicion the

acetyl value should be determined; should this be low the subsequent examination will follow the lines already outlined above, the actual methods depending upon the nature of the results already obtained at this stage. The presence of liquid vegetable oils may be confirmed by an increase in the iodine value or by the presence of oleic acid determined as described above.

Hydrogenated Castor Oil.—When subjected to hydrogenation castor oil can be hardened in the usual way. The hydroxy group can, by suitable means, be either left untouched or completely removed. In the former case the hardened product retains to a considerable extent its special solubility properties, whilst in the latter case these are completely changed with formation of a product having the usual solubilities of a hardened fat.

E. Mellana (*J.S.C.I.*, 1914, 33, 701) has examined a sample of the commercial product "coryphol," which is a hardened castor oil. He found that the substance had melting-point 81°, saponification value 180·5, iodine value 18·5, acetyl value 125, whilst the fatty acids had melting-point 75° and solidifying-point 68°.

A. Brochet (*J.S.C.I.*, 1923, 42, 317A) states that castor oil is completely hydrogenated under a pressure of 11 atmospheres in the presence of reduced nickel at 112°–114° in 90 minutes, the hydrogenated oil having melting-point 86° and iodine value 2. When the product is heated in an open flask it begins to give off hydrogen at 150° and the volume liberated increases as the temperature is raised up to about 280°. The original oil absorbs 70 c.c. of hydrogen per grm., whilst about 40 c.c. per grm. is evolved.

In dealing with hydrogenated castor oil Sudborough has reported difficulty in the determination of the iodine value. In the case of a hardened product having an acetyl value of 72, the iodine value as determined by the Wijs method, was 6·9, whilst the Winkler method gave uncertain results varying from 27 to 84—the Winkler method is evidently unsuitable for such cases.

Thoms and Deckert (*Analyst*, 1921, 46, 139) have isolated from a sample of hydrogenated castor oil (M.Pt. 80°, iodine value 12) a new hydroxystearic acid having melting-point 83° (iodine value 0), whilst A. Bömer (*J.S.C.I.*, 1923, 42, 1232A) has isolated from a similar sample the following glycerides; trihydroxystearin (M.Pt. 89·4°), stearodihydroxystearin (M.Pt. 75°), and distearohydroxystearin (M.Pt. 69·5°).

A. Mailhe (*J.S.C.I.*, 1923, 42, 149A) has found that castor oil passed over heated copper or aluminium turnings undergoes decomposition, the products varying according to the catalyst. Below 600° the hydrocarbons formed are almost entirely of the paraffin series, but above this temperature increasing amounts of aromatic hydrocarbons are produced. Oemanthaldehyde is always formed during the process.

Castor Bean Lipase.—The lipase which is present in the castor bean is becoming of increasing value as the basis of commercial methods of fat splitting. The high price of the seeds militates to a certain extent against their use but the undoubted advantages which the method has, will doubtless lead to its increased use. For fuller particulars of the method the reader is referred to page 14 and to the following papers: Y. W. Jalander (*J.S.C.I.*, 1911, 30, 1321); Falk and Sugiura (*Analyst*, 1914, 39, 553); (*J.S.C.I.*, 1915, 34, 143); A. Blanchet (*J.S.C.I.*, 1914, 33, 428); G. Kita (*J.S.C.I.*, 1918, 37, 312A); Sudborough, Watson and Varma (*J.S.C.I.*, 1920, 39, 340A); A. W. Barton (*J.S.C.I.*, 1920, 39, 340A); Haley and Lyman (*J.S.C.I.*, 1922, 41, 223A); Kita and Osumi (*J.S.C.I.*, 1924, 43, B182); Willstatter and Waldshmidt-Leitz (*J.S.C.I.*, 1924, 43, B639).

Oil of Omphalea Megacarpa, Hemel.—The oil of *Omphalea Megacarpa*, Hemel, has been described by Bolton and Hewer (*Analyst*, 1917, 42, 35). These authors state that the seed consists of an inner yellow oily kernel which is coated with a pith-like skin, the whole being loosely enclosed in a fairly thin, grey-brown friable shell. They weigh about 20 grms. each and contain about 50 per cent. of oil, the kernel, which contains about 65 per cent. of oil, being about 70 per cent. of the seed. The oil is liquid at ordinary temperatures, of a pale straw-colour, without any very pronounced taste and having a slight but not unpleasant odour. The medicinal properties are very similar to those of castor oil and as the dose is smaller, the taste not so unpleasant and the viscosity much less, it may prove a valuable alternative to this oil. Bolton and Hewer report that the physiological properties are said to be inherent in the oil itself, and that they are not due to traces of impurity.

It is quite easy to distinguish this oil from castor oil as the characteristics are quite dissimilar—in particular the oil is optically inactive, not readily soluble in alcohol and its viscosity is much less than that of the latter. The following characteristics were observed by Bolton and Hewer :

Saponification value	192·2
n^{40}	1·4648
Iodine value	115·8
Acid value	0·2
Unsaponifiable matter (per cent.)	0·49
S.G. at 15°	0·922

Turkey Red Oils.—A large quantity of the lower grades of castor oil are used for the preparation of turkey red oils. These oils are used during the preparation of cotton-fibre which is about to be coloured with turkey red. The oils are produced by the action of concentrated sulphuric acid, the acid being run slowly into the oil with constant stirring, the temperature being kept below 35°. The oil is diluted with a small quantity of water and washed with a solution of sodium sulphate until the product gives a clear solution with water.

The sulphonated oil (turkey red oil; other sulphonated oils are sometimes used for the same purpose) is miscible with water in all proportions, the resulting solution lathering like a solution of soap. The sulphonated oil is thrown out of solution by the addition of common salt, mineral acids, sodium sulphate, etc.

The amount of sulphonated acids present may be determined by boiling with dilute hydrochloric acid (1 to 5) for 40 minutes with constant agitation after which the fatty layer is dissolved in ether, and the sulphuric acid in the aqueous layer precipitated and weighed as barium sulphate in the usual manner. The chemistry of turkey red oils is dealt with by M. Tschilikin (*J.S.C.I.*, 1915, 34, 723) and F. Erban (*J.S.C.I.*, 1916, 35, 127); their analysis by Richardson and Walton (*J.S.C.I.*, 1912, 31, 105); C. R. Oberfell (*J.S.C.I.*, 1913, 32, 37; 1914, 33, 41, 266); W. Fahrion (*J.S.C.I.*, 1913, 32, 1118); W. Herbig (*J.S.C.I.*, 1914, 33, 602; 1922, 41, 22A); Goldberg and Zipper (*J.S.C.I.*, 1917, 36, 1184); N. Welwart (*J.S.C.I.*, 1920, 39, 727A); German manufacturers (*J.S.C.I.*, 1921, 40, 551A); J. F. L. Reudler (*J.S.C.I.* 1921, 40, 593A); Anonymous (*Analyst*, 1921, 46, 339).

The analysis of sulphonated oils is dealt with by H. van der Waerden (*J.S.C.I.*, 1925, 44, B290).

Chaulmoogra Oil

The chaulmoogra oil of the *B.P.* is required to be derived from the seeds of *Taraktogenos kurzii*, Kind. For a time there was considerable confusion as to the source of the oil and many observers considered that it was derived from *Gynocardia odorata*. The first systematic examinations of the question were undertaken by Power and Barrowcliffe (*J.C.S.*, 1905, 87, 896) and by Power and Gornall (*J.C.S.*, 1904, 85, 838), who showed that the two oils are really quite dissimilar and that the true chaulmoogra oil is derived, as stated before, from *Taraktogenos kurzii*. This latter plant, being uncertain in growth, has been supplanted to a certain extent by the oil from *Hydnocarpus wightiana*, which is known as " kavatel " oil (Francis, *J.S.C.I.*, 1914, 33, 1097), and other oils of the *Hydnocarpus* species, some of which, as stated by Perkins and Cruz (*Analyst*, 1924, 49, 236), may be as effective or possibly more effective in the treatment of leprosy than chaulmoogra oil. The seeds of the various species are found in Indo-China, Assam, Ceylon and also in the Philippine Islands and various parts of the West Indies. Perkins and Cruz (*loc. cit.*) point out that it is easy to distinguish *Gynocardia* seeds from the others since the radicle of the former is lateral whilst those of both *Taraktogenos* and *Hydnocarpus* are terminal.

The oils are all more or less similar in appearance, being of a soft buttery consistency and slightly yellow in colour. Their most striking property is the high optical activity which is, however, not shared by the oil from *Gynocardia odorata*, which is optically inactive. Perkins and Cruz found great similarity between the oil of *Taraktogenos kurzii* and all the *Hydnocarpus* oils with the exception of *H. alcalæ* which was found to contain a large amount of chaulmoogric acid and little or no hydnocarpic acid.

The composition of the oils has been investigated by several workers; the following table due to Perkins and Cruz (*loc. cit.*) contains practically the whole of the information which has at present been obtained:

Table CCLXVI.—Composition of Chaulmoogra Oils (Perkins and Cruz)

Species.	Chaulmoogric Acid.	Hydnocarpic Acid.	Other Constituents.	Fatty Acids M.Pt. °C.	Fatty Acids Specific Rotary Power.
Gynocardia odorata (pressed oil)	None	None	Gynocardin, linolic palmitic, linolenic oleic	..	None
Hydnocarpus alcalæ	Approx. 90%	None (?)	Palmitic, oleic	59	+53·65
Hydnocarpus alpina	Indicated	Indicated	..	..	..
Hydnocarpus anthelminthica (pressed oil)	Present	Present	Glucoside, oleic, palmitic	42–43	+53·6
Hydnocarpus venerata (pressed oil)	,,	,,	Glucoside	43	+60·9
Hydnocarpus wightiana (pressed oil)	,,	,,	Unknown unsaturated acid	41–44	+60·4
Oncoba echinata (extracted oil)	84·5 %	..	No palmitic, liquid acids, 12 %	..	+52·5
Pangium edule . .	Indicated	Indicated	Unsap. 1·5%, gynocardin, palmitic	18	+3·49 (4·72)
Taraktogenos kurzii (pressed oil)	Present	Present	Glucoside, palmitic acid	44–45	+52·6

A large number of observations have been made on the various types of oils which have been collected into one table by Perkins and Cruz, which table is reproduced below:

TABLE CCLXVII.—CHARACTERISTICS OF CHAULMOOGRA OILS (PERKINS AND CRUZ)

Species.	Yield of Oil from Seeds.	Specific Gravity.	Refrac. Index.	M.Pt. °C.	Specific Rot. Power.	Iodine Value.	Sap. Value.	Acid Value
	%						mg. KOH	mg. K
Gynocardia odorata (pressed oil)	19·5	0·925 at 25°	..	20	nil.	152·8	197·0	4·9
Hydnocarpus alcalæ .	40·8	0·9502 at 30°	1·4770	32	+49·6	93·1	188·9	21·8
Hydnocarpus alpina .	..	0·898 at 100°	1·4709 at 40°	22–26	+49·5	84	207	0·3
Hydnocarpus anthelmintica (pressed oil)	16·3	0·953 at 25°	1·473	24–25	+52·5	86·4	212·0	7·5
Hydnocarpus venerata (pressed oil)	23·3	0·9475 at 30°	1·4770 at 30°	19–20	+52·0	99·1	200·3	24·7
Hydnocarpus wightiana (pressed oil)	32·4	0·958 at 25°	.. ..	22–23	+57·7	101·3	207·0	3·8
Oncaba echinata (extracted oil)	47	0·898 100°/15·5°	..	35–45	+48·8	99·7	192·4	4·5
Pangium edule . . .	6·1	0·9049 (0·9092)	1·4665	2	+4·28 (20·65)	113·1	190·3	2·9
Taraktogenos kurzii (pressed oil)	30·9	0·951 at 25°	1·476	22–23	+52·0	103·2	213·0	23·9

Perkins and Cruz have themselves investigated the characteristics of a number of oils of various species as well as those of a number of commercial oils—these are given in Table CCLXVIII.

Lifschutz (*Analyst*, 1922, 47, 125) describes a colour reaction which is produced when 4 to 5 drops of strong sulphuric acid are added to a solution of 1 drop of the oil in 0·5 c.c. of chloroform and 1·5 c.c. of glacial acetic acid. An intense grass-green colouration is produced whilst the solution is red-violet by transmitted light and has a characteristic spectrum. He states that freshly prepared oil does not give the reaction, but that it does after oxidation with benzoyl peroxide.

Dean and Wrenshall (*Analyst*, 1921, 46, 52; *J.S.C.I.*, 1925, 44, B928) have shown that it is not possible to separate chaulmoogric and hydnocarpic acids by fractional precipitation or crystallisation. They further found ethyl alcoholysis to be less satisfactory than direct distillation which was adopted, followed by recrystallisation from 80 per cent. alcohol for chaulmoogric acid and petroleum spirit for hydnocarpic acid. Full details of the separation are given. (Cf. also T. Hashimoto, *J.S.C.I.*, 1925, 44, B889.)

As already pointed out, the optical activity is the most striking feature of the fat (see Cardamom fat, page 410) and this will naturally be the main test on which reliance will be placed. The *B.P.* has the following requirements for the oil:

"A brownish-yellow oil or soft fat. Characteristic odour; taste somewhat acrid. Melting-point about 22 to 30. Specific gravity at 45 about 0·940; saponification value 198 to 213; iodine value 96 to 104; acid value 21 to 27. Soluble in ether, in chloroform, and in carbon disulphide; partially soluble in cold alcohol (90 per cent.); almost entirely soluble in hot alcohol (90 per cent.)."

TABLE CCLXVIII.—CHARACTERISTICS OF CHAULMOOGRA OILS (PERKINS AND CRUZ)

Sample.	Sp. Gr. $\frac{30°\text{ C.}}{30°\text{ C.}}$	Refrac. Index n_D^{30}.	Freez. Point. °C.	Rot. 100 mm $30°/_D$.	I.V. Hanus.	Sap. Val.	Acid as % Oleic.	Fatty Acids Freez. Point °C.	Fatty Acid Spec. Rotatory Power. $[\alpha]_D^{30}$.
Gynocardia odorata .	0·929	1·4743	4	+0	160	198	2·7	20	+0
Hydnocarpus alcalæ C.	0·948	1·4763	24	+48·3	94·0	202	6·7	55	+40
Hydnocarpus anthelminthica . . .	0·952	1·463	16	+44·2	84·5	201	3·6	36	+50
Hydnocarpus hutchinsonii	0·943	1·4743	23	+44	83·5	199	5·3	43	+50
Hydnocarpus subfalcata A . .	0·951	1·4761	21	+49·1	89·0	206	6·6	41	+36
„ B . .	0·956	1·4770	15	+51·6	91·5	205	6·2	34	+55
Hydnocarpus venerata . . .	0·947	1·4769	20	+46·4	90·7	191	1·2	47	+49
Hydnocarpus wightiana A . .	0·947	1·4763	11	+51·2	97·0	207	6·7	40	+54
B . .	0·950	1·4772	13	+50·1	99·1	204	6·3	39	+54
C . .	0·948	1·4769	11	+51·4	101	204	15·1	35	+56
Hydnocarpus woodii .	..	1·473	18	+45·9	68·5	192	5·9	43	+53
Pangium edule, B :									
Fresh . .	0·925	1·472	7	+16·9	78·5	200	6·9	18	+17
Rancid . .	..	1·467	4	+2·8	75·0	181	21	17	+2
Taraktogenos kurzii:									
A . .	0·951	1·4771	9	+43·5	104	215	3·4	32	+43
B . .	0·948	1·4769	9	+45·1	105	199	14·8	36	+50
C . .	0·948	1·4765	14	+51·2	102	203	18·8	39	+58
D . .	0·946	1·4753	20	+47·9	95	203	5·5	32	+52
E . .	0·946	1·4753	20	+47·5	95	204	4·5	28	+51
F . .	0·947	1·4763	10	+46·7	104	197	13·0	21	+51
G . .	0·948	1·4764	8	+46·2	97	203	22·6	28	+51
H . .	0·951	1·4767	9	+45·9	102	198	13·8	29	+49
I . .	0·949	1·4762	18	+46·3	96	187	14·9	22	+48
K . .	0·952	1·4770	5	+45·7	105	204	14·6	26	+47
L . .	0·948	1·4768	5	+45·1	104	205	12·6	23	+48
M. .	0·950	1·4762	7	+44·9	102	204	15·5	24	+48

For further particulars the following authors may be consulted: P. Chattopadhyay (*J.S.C.I.*, 1915, 34, 1102); F. B. Power (*J.S.C.I.*, 1915, 34, 1214) who criticises the contentions of the previous author, Rakuzin and Flier (*J.S.C.I.*, 1916, 35, 366); Brill and Williams (*Analyst*, 1918, 43,

139); V. Cofman (*Analyst*, 1919, 44, 371); G. A. Perkins (*J.S.C.I.*, 1922, 41, 996A); S. Keimatsu (*Analyst*, 1921, 46, 52); A. Marcan (*Analyst*, 1924, 49, 88); O. Shöbl (*Analyst*, 1924, 49, 241; cf. *J.S.C.I.*, 1924, 43, B995). Cf. *Hydnocarpus anthelmintica* (*J.S.C.I.*, 1918, 37, 166A); *Hydnocarpus wightiana* (*J.S.C.I.*, 1914, 33, 1097; 1923, 42, 562A); *Hydnocarpus alpinus* (*J.S.C.I.*, 1913, 32, 96).

Croton Oil

Croton oil is obtained from the seeds of *Croton tiglium*, a plant which is cultivated in the Far East. The colour varies from a light to a reddish brown, the oil is viscid and slightly fluorescent. The oil has a very unpleasant odour, an acrid burning taste and blisters the skin and mucous membrane. It acts as a very powerful purgative, the dose being about 0·05 c.c., but these properties disappear on hydrogenation.

The oil has been examined by various observers as Dunstan and Boole (*J.S.C.I.*, 1895, 14, 985), Dulière (*ibid.*, 1899, 18, 1133), and Lewkowitsch (*Analyst*, 1899, 24, 319).

Croton oil is miscible with half its volume of alcohol, but on the addition of more alcohol separation into two layers takes place; it is completely soluble in petroleum ether (cf. castor oil). The oil is strongly dextro-rotatory and contains notable proportions of volatile fatty acids. For a colour test, cf. Comte, *Analyst*, 1916, 41, 275. The following are the usual variations in the characteristics:

Specific gravity 15°/15°	0·937–0·950 *
Saponification value	200–215
Iodine value	102–108
Reichert value	12·0–13·6
Polenske value	1·2 †
n^{40}	1·4700–1·4730
Titre ° C.	19

The B.P. states that the oil should thicken slightly but not solidify, either completely or partially, when vigorously shaken with half its volume of fuming nitric acid and the same proportion of water showing that other non-drying oils are absent.

Curcas Oil

Curcas oil (also known as purging-nut oil or physic-nut oil) is obtained from the seeds of the purging-nut (*Jatropha curcas*), which is cultivated in various parts of Central America but for the most part in the Cape Verde and Comoro Islands. The seeds weigh about 0·5 grm. each and consist of about two-thirds kernel of which about 50 per cent. is oil (*J.S.C.I.*, 1918, 37, 63A).

According to C. Grimme (*ibid.*, 1921, 40, 778A) the oil consists of the glycerides of palmitic, myristic and curcinoleic acid, the latter being a hydroxy acid analogous to ricinoleic acid. The seeds contain a highly poisonous substance, curcin. The oil has powerful purgative properties which are considerably greater than those of castor oil; it may also act as an emetic. The oil has quite marked drying properties (*Analyst*, 1922, 47, 125) and is, therefore, not suitable as a substitute for castor oil for lubrication purposes neither has it the viscosity of this latter oil. The toxic properties of the oil have been dealt with by J. Felke (*J.S.C.I.*, 1914, 33, 651).

* *B.P.*, 0·940-0·960. † Elsdon and Hawley (*Y.B.P.*, 1913, 573).

The following characteristics have been observed for this oil:

TABLE CCLXIX.—CHARACTERISTICS OF CURCAS OIL

	[2] Lewkowitsch.	Grimme.	[1] Imperial Institute.
Specific gravity 15°/15°	0·919–0·921	0·921	0·919
Melting-point °C.	−4	−5 to −6	..
n_D^{40}	1·4636	1·4618	..
Saponification value	193·2	189·2	191·6
Iodine value	98–105	98·8	98·7
Reichert value	0·6	0·7	0·4
[3] Acetyl value	8·4–9·8	8·9	25·4
Acid value	0·6–8·5	3·2	4·5
Titre °C.	28·6	..	28·7
Unsaponifiable matter	0·5–0·6	0·7	..

[1] Gold Coast seed. [2] Cf. *J.S.C.I.*, 1893, 12, 453, 935. [3] L. Archbutt, *J.S.C.I.*, 1898, 17, 1010.

The seeds of *J. mahafalensis* have been examined by H. Bimar (*J.S.C.I.*, 1912, 31, 1040). The seeds contain about 75 per cent. of kernels which contain 60 per cent. of oil and which yield 44·5 per cent. of oil on expression. The properties were similar to those of curcas oil and the following characteristics were determined:

Specific gravity 15°/15°	0·921
Titre test °C.	21
Saponification value	194
Iodine value	111·8
Acid value	17·6
Acetyl value	17·0
n^{40}	1·4575

CHAPTER XXX

ROSIN AND ROSIN OILS

Rosin or colophony is the solid residue left when turpentine is distilled for the preparation of oil of turpentine—the latter being the ordinary " turpentine " or " turps " of commerce. It has specific gravity 1·070 to 1·080, acid value 150 to 180, and saponification value somewhat higher than the acid value. (Cf. C. Lüdecke, *J.S.C.I.*, 1914, 33, 302.) It consists therefore for the most part of organic acids (" resin acids ") which fact may be made use of for its determination under certain circumstances. It should be almost entirely soluble in petroleum ether and in industrial methylated spirits.

When rosin is subjected to destructive distillation rosin spirit and rosin oil are produced. Rosin spirit (light rosin oil) consists of the fractions boiling between 150° and 200° and has specific gravity about 0·880—it consists largely of mixtures of various types of hydrocarbons.

Rosin oil (heavy rosin oil) has a specific gravity of from 0·97 to 1·00. Refined oils do not usually exceed 0·99, but certain samples have been known to have a gravity greater than 1·0. The oil is strongly dextro-rotatory, having $[\alpha]_D^{20} = +30°$ to $+60°$. The oil has a remarkably high index of refraction, $n_D^{40} = 1{\cdot}525 - 1{\cdot}545$, whereas mineral oils have figures usually much lower than this, e.g., 1·470–1·485. Highly refined oils are usually free from acidity and have little or no saponification value. The iodine value of crude oils is mostly over 100, but in refined oils is about 40 to 50. Rosin oils have a distinct tendency to dry which is increased by the presence of driers.

The Determination of Rosin Acids in Fatty Acids.—The most suitable method for the determination of rosin acids in fatty acids is that of Twitchell (*J.S.C.I.*, 1891, 10, 804) which depends upon the fact that the former do not combine with ethyl alcohol to form esters as do the latter when treated with an alcoholic solution of hydrochloric acid; the residual rosin acids, after removal of the hydrochloric acid, being determined by titration with sodium hydroxide to phenolphthalein. The method may be carried out either volumetrically or gravimetrically, the former method being probably more accurate, but usually giving results a little too high, whilst the latter are often low. The methods may be carried out in the following way as suggested by C. A. Mitchell :

Gravimetric Method.—From 2 to 3 grms. of the mixture of fatty acids and rosin are dissolved in 10 times their volume of absolute alcohol in a flask, and dry hydrochloric acid gas introduced in a moderate stream. The flask is set in a vessel with water to keep it cool. The acid is rapidly absorbed, and, after about 45 minutes, the esters separate, floating in the solution, and no more hydrochloric acid is absorbed. The current of gas is now stopped, and the flask allowed to stand for half an hour to complete the reaction. The liquid is diluted with about 5 times its volume of water and boiled until the acid solution is clear, the esters, with rosin in solution, floating on the top. To this is added some petroleum spirit, and the whole transferred to a separating funnel, the flask being washed out with petroleum spirit. The acid solution is then run off, and the petroleum spirit solution (which ought to measure about 50 c.c.) washed once with water and then shaken in a funnel with a solution of 0·5 grm. of potassium hydroxide and

5 c.c. of alcohol in 50 c.c. of water. The rosin is immediately saponified and the two layers completely separated. The solution of rosin soap can be run off, treated with acid, the rosin collected in any manner desired, dried, and weighed. A second washing of the soap with petroleum spirit is hardly necessary, as very little remains after the first extraction.

Volumetric Method.—The first stages of the volumetric method are similar to the gravimetric, with the exception that the contents of the flask are washed into the separating funnel with ether instead of petroleum spirit, and the ethereal solution in the funnel is then thoroughly washed with water until the wash-water is no longer acid; 50 c.c. of alcohol, previously neutralised, are then added and the solution titrated with standard sodium hydroxide solution with phenolphthalein as indicator.

Twitchell (*loc. cit.*) and Lewkowitsch (*J.S.C.I.*, 1893, 12, 504) both found that 1 c.c. of N/1 NaOH is equivalent to about 0·346 grm. of rosin, but Mitchell finds that occasionally considerable divergencies from this may take place.

W. Fahrion (*ibid.*, 1911, 30, 1266) has proposed the following modification : The rosin and free fatty acids existing in the fat are extracted by dissolving 5 grms. of the fat in a mixture of 50 c.c. of petroleum spirit and 20 c.c. of 90 per cent. alcohol, adding N/1 alkali in presence of phenolphthalein until a red colour is obtained, and diluting with water until the alcohol is of 60 per cent. strength. The soap solution is treated with 1 c.c. of N/1 alkali and the alcohol evaporated on a water-bath. The mixed rosin and fatty acids are obtained by acidifying and shaking out with ether in the usual way. Esterification is carried out by treating the mixed acids with 20 c.c. of absolute alcohol and shaking the solution vigorously with 20 c.c. of petroleum spirit and 1 c.c. of concentrated hydrochloric acid. Should a separation occur, absolute alcohol is added until a homogeneous liquid is obtained. Esterification becomes complete by allowing the solution to stand overnight, when phenolphthalein and N/1 alkali are added until a red colour is just obtained. The solution is diluted with water till the alcohol is of 60 per cent. strength and from the alcoholic solution of rosin soap the rosin acids are obtained as in the original method.

Leiste and Stiepel (*ibid.*, 1914, 33, 1099) detect rosin in soap or fat by dissolving in alcohol, neutralising with alcoholic soda and evaporating the solution with freshly ignited sand. The rosin may be extracted from the residue with acetone containing 2 per cent. of water.

Wolff and Scholze (*Analyst*, 1914, 39, 228) state that they found that their method, given below, gave better results than those of either Twitchell or Fahrion :

From 2 to 5 grms. of the mixture of fatty and rosin acids are dissolved in 10 to 20 c.c. of absolute methyl alcohol, and the solution treated with 5 to 10 c.c. of a solution of 1 part of sulphuric acid in 4 parts of methyl alcohol, and boiled for two minutes under a reflux condenser. The liquid is then mixed with 5 to 10 times its volume of 7 to 10 per cent. sodium chloride solution, and the fatty acid esters and rosin acids extracted with ether, or a mixture of ether and petroleum spirit. The united extracts are washed with dilute sodium chloride solution, alcohol added, and the mixture titrated with N/2 alcoholic potassium hydroxide solution. A mean acid value of 160 is taken for the rosin acids, and a correction of 1·5 per cent. allowed for fatty acids that have escaped esterification. The percentage of rosin acids is then obtained by the formula

$$X = \frac{a \cdot 17 \cdot 76}{m} - 1 \cdot 5,$$

where *a* represents the number of c.c. of potassium hydroxide solution, and *m* the weight of the mixture taken. The result multiplied by 1·07 gives approximately the amount of rosin.

None of the above methods will give accurate results, but any one will give practical information. The inexperienced worker should always compare the results obtained from an unknown sample with others of known composition examined under identical conditions. (Cf. R. Jungkunz, *J.S.C.I.*, 1925, 44, B556; G. de Belsunce, *ibid.*, page B929; J. Davidsohn, *Analyst*, 1925, 50, 356.)

Rosin may be detected by means of the Liebermann-Storch test, described on page 79; it should not be overlooked that the same reaction is given by cholesterol.

For the metal content of some metallic rosinates see L. G. Radcliffe (*J.S.C.I.*, 1915, 34, 644).

CHAPTER XXXI

HYDROGENATED OILS

The Recognition of Hydrogenated Oils.—The recognition of hydrogenated oils as a class is not always easy when they are present in admixture with other fats. The recognition of the particular source of the hydrogenated product is frequently impossible for the simple reason that there are little, if any, differences in the composition of such fats from various sources after the process of hydrogenation has been continued past a certain stage.

When the use of such oils first became general the most useful method of detection was that which depended upon the recognition of the small amounts of nickel which remained in the oil on completion of the process. This may be carried out in the following manner due to F. W. Atack (*Analyst*, 1913, 38, 316).

The nickel may be separated from the fat either by igniting or by extracting the oil with boiling hydrochloric acid, evaporating the acid liquid and igniting. As the amounts of nickel present are usually very small it is desirable to take as much fat as possible quantities of 100 grms. or so being quite suitable. The residue obtained by either of these processes is treated with dilute hydrochloric acid and then a drop of nitric acid and the solution evaporated until almost dry. Excess of ammonia is then added and afterwards a 0·02 per cent. solution of α-benzildioxime in alcohol when in the presence of traces of nickel a rose-red colour is produced. The amount of nickel found varies from 0·00001 to 0·001 grms. per 100 grms. of oil, but it is not infrequently absent altogether.

The use of α-benzildioxime in this manner is to be preferred to that of dimethylglyoxime which was suggested by Bömer and Leschly-Hansen (*Chem. Rev. Fett. Ind.*, 1912, 19, 218, 247) in that the latter has been found by F. Prall (*J.S.C.I.*, 1915, 34, 237) to give a somewhat similar reaction with certain pure untreated oils unless the organic matter was removed by ignition whilst it is at the same time somewhat less delicate than the former. On account of the possible uncertain results given by these organic reagents A. W. Knapp (*Analyst*, 1913, 38, 102) prefers to dissolve the residue after treatment with hydrochloric acid in one drop of water and test with one drop of ammonium sulphide solution on a white tile.

Tortelli and Jaffe (*J.S.C.I.*, 1914, 33, 1061) obtained a yellowish-pink colour changing quickly to green with hydrogenated marine animal oils by dissolving 5 c.c. of the molten fat in 10 c.c. of chloroform, adding 1 c.c. of glacial acetic acid and then shaking with 2·5 c.c. of a 10 per cent. solution of bromine in chloroform. This test is reported upon unfavourably by J. Davidsohn (*ibid.*, 1916, 35, 186) but M. Tsujimoto (*ibid.*, page 262) states that most marine animal oils when fresh give the reaction, although it fails frequently when the oils are old; hydrogenated fish oils give indistinct colourations, whilst vegetable oils and terrestrial animal oils do not give any reaction at all.

There have been many suggestions for the detection of hydrogenated oils by means of those glycerides which are less soluble in ether or in some other organic solvent (see page 5). These tests are really methods for the isolation of glycerides containing stearic and other solid acids (cf. J. Leimdorfer,

ibid., 1914, 33, 206) so that they will not of necessity differentiate between hydrogenated liquid oils and tallow, particularly in mixtures (cf. *A.O.A.C.*, *Analyst*, 1923, 48, 225; K. Amberger, *J.S.C.I.*, 1916, 35, 1077) except in those cases where the ordinary characteristics convey the information of themselves. Norman and Hugel depend upon the isolation of arachidic acid (*ibid.*, 1917, 36, 658) by crystallising the fatty acids from alcohol the relative proportions of stearic and arachidic acids being determined from the neutralisation value of the isolated product. A. Grun (*ibid.*, 1919, 38, 729A) suggests that the method of alcoholysis (page 51) might assist, but this is not suitable for routine work, although in cases of great importance it might be of help.

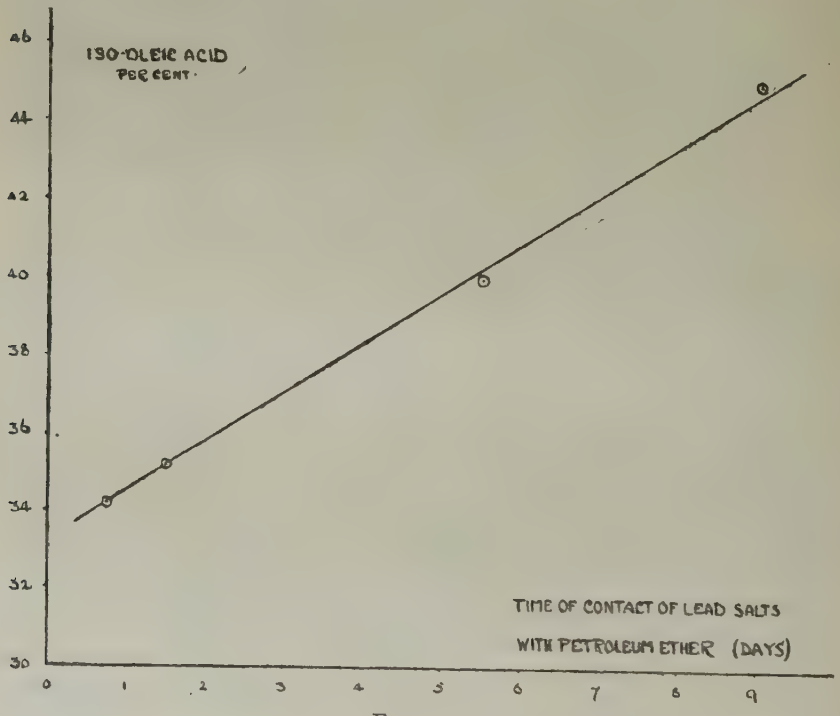

FIG. 10.

[*By permission of Williams & Bolton and The Analyst*

The unsaponifiable matter has been suggested as a possible method of attack (cf. whale oil, page 448), but the most useful method would appear to be that based upon the fact that hydrogenated fats do not show the same relationship between their chemical and physical properties as do natural fats (cf. T. Arentz, *J.S.C.I.*, 1920, 39, 304A). This is brought about by the fact that during the process of hydrogenation certain isomers of oleic acid are apparently formed the properties of which are quite different from natural oleic acid and from most of the unsaturated fatty acids (erucic acid is somewhat of an exception). These new acids have been termed by Myddleton and Barry (*Fats: Natural and Synthetic.* London 1924). "New acids of hydrogenation" and by other observers "iso-oleic" acid. This new iso-oleic acid should, however, be carefully distinguished from the substance previously known by that name.

This new isomer or mixtures of isomers (their constitution is fully discussed by C. W. Moore, *J.S.C.I.*, 1919, 38, 320T) of oleic acid is isolated along with the solid acids in all the usual methods for separating solid and liquid acids so that in those cases where the solid acids have a high iodine value and rape oil is absent hydrogenated fats may be deduced.

The process has been worked out by Williams and Bolton (*Analyst*, 1924, 49, 460) who separate the solid acids either by the lead-salt-ether method of Gusserow-Varrentrapp (page 45) or by the lead-salt-alcohol method of Twitchell, *Analyst*, 1921, 46, 466, page 46. The following abstract of this paper shows how the results are to be interpreted.

If the oil contains no hydrogenated oil the iodine value of the solid fraction will be not greater than 5 units (due to incomplete removal of unsaturated liquid acids in washing). If hydrogenated fat be present to any extent, this iodine value will be higher owing to the presence of iso-oleic acid, the content of which is calculated from this iodine value.

Allowing 5 units of iodine value in the solid fraction due to incomplete washing, the proportion of iso-oleic acid in the total fatty acids from the oil is given by the expression

$$\text{Percentage of iso-oleic acid} = \frac{95}{100} \times S \times \frac{I-5}{90}.$$

Where S = percentage of solid fraction obtained, and I = its iodine value.

The liquid fraction in each case contains the unsaponifiable matter of the fat. In a complete determination of the composition of the fatty acids this would have to be estimated and an allowance made for its effect on the iodine value of this fraction.* The solid fraction will be free from unsaponifiable matter and if only the proportion of iso-oleic acid is to be estimated, no correction is necessary.

Most commercial hydrogenated oils used in edible products have iodine values lying between 50 and 70 units and contain from 30 per cent. to 35 per cent. of iso-oleic acid, from which figures the approximate proportion of hydrogenated oil in the mixture may be deduced.

A drastic change in the composition of hydrogenated oils has recently resulted from a modification of the methods employed, by the introduction of a continuous process, whereby a flow of oil passes through a relatively large mass of catalyst. The process can be operated so as to produce

(*a*) the normal proportion of iso-oleic acid in the product; or (*b*) a reduced amount.

It will be obvious that the control of the proportion of iso-oleic acid on a commercial scale militates against the accuracy of the deductions made from the process the use of which the authors have suggested, with the result that in cases where the method of hydrogenation employed is unknown, the proportion of hydrogenated oil may be largely over-estimated. The value of the process for the actual detection of hydrogenated oil remains, however, unaltered.

The curve shown in the figure has been prepared by Williams and Bolton (*loc. cit.*). It shows what may be taken as average proportions of the various fatty acids contained in samples of hydrogenated oils of varying iodine values and from varying sources.

Characteristics of Hydrogenated Oils.—The properties of many of the hydrogenated oils have been given in the monographs on the original oils.

* Such determinations are described in full in *Fats: Natural and Synthetic.* Myddleton and Barry, p. 114.

Further figures are given here on a number of commercial and other samples which have been examined from time to time.

The main indications showing to what stage the hydrogenation has been carried are the melting-point and the iodine value, there being quite a close relationship between these two figures. In general, hydrogenation has little effect on the saponification value, but progressively lowers the iodine value and the refractive index, whilst the melting-point is raised.

Bömer and Leschly-Hansen (*J.S.C.I.*, 1912, 31, 996) give the following typical results for hydrogenated oils from the sources named. These and the following figures must be taken merely as typical examples of useful products likely to be met with in commerce and are in no way indicative of the source from which they are obtained.

TABLE CCLXX.—CHARACTERISTICS OF HYDROGENATED OILS

Original Oil.	M.Pt. °C.	Sol. Pt. °C.	n^{40}.	Acid Value.	Sapon. Value.	Iodine Value.
Arachis	51·2	36·5	1·4594	1·0	188·7	47·4
Sesamé	47·8	33·4	1·4603	0·5	190·6	54·8
Cotton-seed . . .	38·5	25·4	1·4618	0·6	195·7	69·7
Whale	45·1	33·9	1·4587	1·2	192·3	45·2
Coconut	44·5	27·7	1·4494	0·4	254·1	1·0

E. Mellana (*J.S.C.I.*, 1914, 33, 701) has published the following figures including three for the commercial products "Talgol," "Candelite" and "Coryphol."

TABLE CCLXXI.—CHARACTERISTICS OF HYDROGENATED OILS

	M.Pt. °C.	M.Pt. of Fatty Acids. °C.	Sol. Pt. of Fatty Acids. °C.	Sap. Value.	Iodine Value.	Acetyl Value.	n^{60}.
Hydrogenated :							
Cotton-seed oil .	59	57	50·3	192·3	41	..	..
Soya-bean oil . .	68	66	61·2	190·9	15·2	..	..
Kapok-seed oil .	55	53	48	191	32	..	1·4537
Whale oil . . .	52·5	49	44	169·6	28·8	..	1·4517
Sperm oil . . .	50	48	39	131·7	17·3	..	1·4445
Talgol.	43	41	35·7	190·2	61·3	14	..
Candelite	55	54	50·4	191	4	..	..
Coryphol	81	75	68	180·5	18·5	125	..

Sudborough, Watson and Athawale (*J.S.C.I.*, 1923, 42, 103A) state that for hardened cotton-seed, linseed, arachis, mohua, sesamé and sardine oils the relationship between the iodine value and the refractive index is independent of the time and of the type of catalyst used and is very similar for the various oils. It may be represented with an accuracy of about 0·0005 by the equation

$$n_D^{60} = 1{\cdot}4468 + 1{\cdot}03 \times 10^{-4}(\text{I.V.}) + 7{\cdot}3 \times 10^{-8}(\text{I.V.})^2$$

the figure 1·4468 being the refractive index of the oils when completely hardened. Hardened coconut oils (*vide supra*) have a much lower refractive index than other oils having the same iodine value. The following glycerides were isolated in a pure state from hardened castor oil. Trihydroxystearin, M.Pt. 89·4°; stearodihydroxystearin, M.Pt. 75°; distearohydroxystearin, M Pt. 69·5° C.

The characteristics and composition of the natural oils after varying degrees of hydrogenation have been studied at length by Myddleton and Barry and published by these authors in their work *Fats : Natural and Synthetic*; reference should be made to this for complete information on the subject. Their curves for variation between the iodine value and the melting-point and refractive index respectively for hydrogenated linseed oil are here reproduced. Their Figs. 11 (*a*) and 11 (*b*). The following table, due also to these authors, compares the melting-points of certain natural and synthetic fats having the same iodine value.

TABLE CCLXXII.—COMPARISON OF MELTING-POINTS OF NATURAL AND HYDROGENATED FATS (MYDDLETON AND BARRY)

Fat.	Iodine Value.	Melting-point. °C.	Ellis' Melting-point. °C.
Lard	58·6	47–40	..
Hardened linseed oil	58·6	49	..
,, cotton seed	58·6	41·6	46
,, whale oil	58·6	39·1	..
Beef tallow	35·8	43–44	..
Hardened linseed	35·8	57	..
,, cotton seed	35·8	51	54
,, whale oil	35·8	47·5	..
Mutton tallow	42·5	45	..
Hardened linseed	42·5	55	..
,, cotton seed	42·5	48·2	52
,, whale oil	42·5	45·4	..

Hydrogenated Oils as Food.—In the present state of our knowledge of dietetics it is not possible to be at all definite as to the food-value of hydrogenated oils. On one point only can any definite opinion be given and that is that under no circumstances should attempts be made to introduce such artificial materials into commerce as articles of diet without due notice being given to the purchaser of the character of the material being sold. The recent work on accessory food factors (no matter what the ultimate outcome of such work may be) renders it possible that there may be material, if minute, differences between a synthetic body and the natural product which it is intended to simulate, and it is most desirable both on the score of ethics and of public health that purchasers should be fully acquainted with the nature of the product they are buying. Some manufacturers state that deception of the public is not undesirable so long as they suffer no actual harm—since their prejudices may force them to refuse perfectly good articles;

the doctrine is dangerous, particularly if the manufacturer is to be the sole arbiter as to what is, and what is not, a wholesome article.

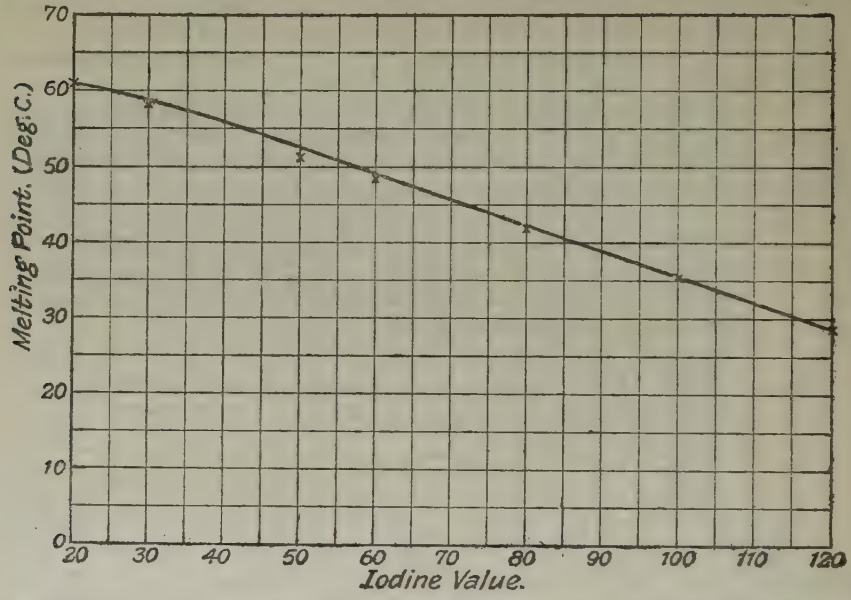

FIG. 11 (*a*).—Hydrogenated linseed oil. Variation of melting-point with iodine value (Myddleton and Barry)

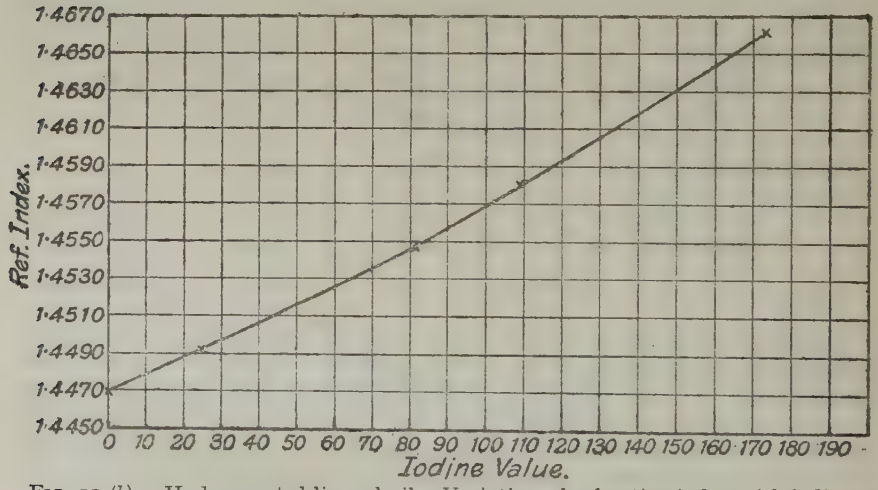

FIG. 11 (*b*).—Hydrogenated linseed oil. Variation of refractive index with iodine value (Myddleton and Barry)

The food value of hydrogenated oils falls roughly under three heads : firstly, their digestibility; secondly, their content of growth promoting properties; and thirdly, the possible presence of minute traces of the metallic substances which are used as catalysts.

Digestibility.—The question of the digestibility of hydrogenated oils is to a large extent a question of melting-point and in this connection it

must be remembered that such materials of high melting-point are not likely to be used of themselves but in admixtures with others so that the melting-point of the whole will usually be below body temperature. C. F. Langworthy (*Analyst*, 1923, 48, 232) has conducted feeding experiments on men using twenty-three animals' fats, thirty-four vegetable fats, and six hydrogenated fats which were administered in the form of cornflour pudding. He states that there appears to be little difference in the digestibility, but that those having melting-points above the body temperature appear to be not quite so thoroughly assimilated.

Holmes and Deuel (*ibid.*, 1921, 46, 503) conducted similar experiments with hydrogenated oils of various melting-points and found the following results:

TABLE CCLXXIII.—DIGESTIBILITY OF HYDROGENATED OILS (HOLMES AND DEUEL)

Cotton Seed Oil.		Arachis Oil.		Maize Oil.	
M.Pt. °C.	Digestibility per cent.	M.Pt. °C.	Digestibility per cent.	M.Pt. °C.	Digestibility per cent.
35	96·8	37	98·1	33	94·7
38·6	95·5	39	95·9	43	95·4
46	94·9	..	..	50	88·5
..	..	43	96·6	..	..
..	..	50	92·0	..	..
..	..	52	79·0	..	..

Myddleton and Barry (*loc. cit.*) report that a large-scale experiment on 250 people under medical observation in Germany showed that a diet containing 23 per cent. hydrogenated whale oil was satisfactorily assimilated, and no deleterious effects on the subjects were observed.

In these experiments the percentage assimilated never fell below the value for butter fat by more than 10 per cent. (Cf. W. Fahrion, *J.S.C.I.*, 1919, 38, 510A.)

Vitamines.—The question of the effect of hydrogenation upon any substances present in natural oils and fats which are essential to nutrition is a difficult one. It has been proved that in many cases such substances (or the properties of the oil that are ascribed to them) are entirely destroyed during the process. In the case of oils which are originally extremely active it has been found that in some circumstances the hydrogenated product is still active, thus Zilva (*J.S.C.I.*, 1924, 43, 962B) has shown that cod-liver oil hardened under strictly anærobic conditions at a temperature of 150° for 1–2 hrs. and deodorised by treatment with steam was found to be as active as the original oil. Partially hardened cod-liver oils still in a liquid condition, and free from the unpleasant fishy taste and smell, were also found to retain their original activity.

Some recent work of L. S. Fridericia (*J.S.C.I.*, 1925, 44, B144) seems to show that the addition of hydrogenated whale oil to a diet of which the vitamin A was supplied by butter fat rendered the diet insufficient for growth of rats, although the hydrogenated oil itself was shown to be without toxic effect; no such inactivation was observed with hydrogenated coconut or hemp-seed oils or with non-hydrogenated coconut oil or abdominal fat

from the pig; if, however, the latter fat were first heated to 105° in thin layers for 24 hrs. with free access of air, it acquired an inactivating action towards vitamin A; it is suggested that in this case the inactivating action may be due to the formation of peroxides in the heated fat.

These observations are interesting and are of such importance that further work along the same lines will doubtless follow immediately. (Cf. *Analyst*, 1925, 49, 146.)

The amount of work that has been done up to the present is inconclusive and although it is not, perhaps, possible to say that hydrogenation is definitely objectionable in the case of edible fats, yet it cannot be said with certainty that hydrogenated whale oil is the dietetic equal of butter fat or even of beef fat (but cf. Thoms and Muller, *J.S.C.I.*, 1920, 39, 131A).

Catalysts.—The importance of the possible effect of the catalyst upon the human organism is not now of such moment as it once was on account

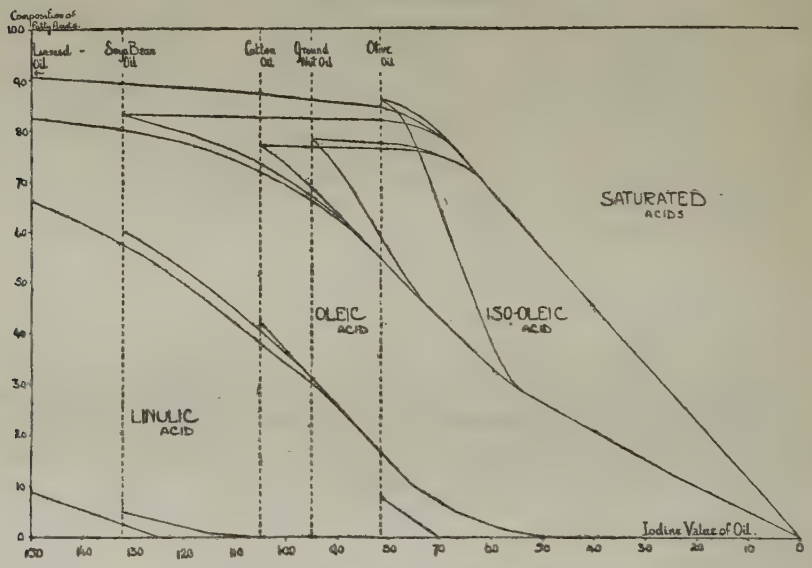

FIG. 12.—Composition of hydrogenated oil.

[*By permission of Williams & Bolton and The Analyst*

of the fact that only mere traces of the catalyst now remain, whilst in some cases the whole of it is removed. Numerous workers have written upon the point, the general opinion being that the quantities of, say, nickel, likely to be found in a hydrogenated oil are quite immaterial and harmless, in fact Bordas (*J.S.C.I.*, 1919, 38, 787A) has stated that quantities of nickel up to 0·5 grm. of NiO per day for 52 days are without injurious effect.

K. B. Lehmann (*ibid.*, 1914, 33, 763) has stated that commercial samples of hydrogenated arachis, sesamé and cotton-seed oils contained from 0·07 to 6 mg. Ni per kilo. Feeding experiments with these fats were made upon animals and human beings for periods up to six months without any ill effects being felt or observed.

At the present time, for various reasons, the amounts of hydrogenated oils in use are not large but their extended use is mostly a question of economic value and is quite possible at any time.

For the preparation of hydrogen for use in the hydrogenation of oils, cf. *Ind. Chem.*, 1925, 1, 149.

APPENDIX I

VITAMINES

It is quite outside the scope of the present work to give any detailed account of the so-called vitamins (for this the reader is referred to the excellent summary on the subject due to A. Harden which is published by H.M. Stationery Office for the Medical Research Council), but a brief statement of the main points which are of interest to the oil chemist may not be out of place. It should, however, be definitely stated that our knowledge of these substances is still small and that they have not yet been isolated as individuals although very considerable progress has been made along these lines quite recently. A complete definition is impossible, but they may be looked upon as food constituents, present in minute proportions in certain foods, which are (or seem to be) absolutely necessary for nutrition; without them, no matter how chemically complete the diet may be, an animal cannot grow and thrive.

Up to the present time considerable evidence has been adduced to prove the existence of three such substances, whilst the possibility of the existence of others is not remote. The three for the existence of which the evidence is most complete are fat-soluble A, water soluble B—the anti-neuritic vitamin, and vitamin C—the anti-scorbutic vitamin; deficiency of the latter two appear to produce beri-beri and scurvy respectively.

From the point of view of oils the only one which is of immediate interest is fat soluble A which seems to have some intimate connection with growth. This factor is contained in the largest amounts in the liver oils of certain fish such as the cod and also in many other oils of animal original such as beef fat, butter fat, etc. Vegetable oils in general contain only small amounts, if any. Lard as a general rule contains little, if any, but at least a portion of this deficiency is caused by the methods of manufacture.

It would appear that the primary source of the fat soluble A is the green leaves of plants, animal fats derive their supplies either directly or indirectly from this source. The diet of the animal has a great if not a complete effect upon the amount of this constituent found in the fat. Drummond, Coward and Watson (*J.S.C.I.*, 1921, 40, 746A) have shown that winter butter is very deficient in this material but that as soon as the cows are put out to grass the amount increases. It is quite possible that some of the marine diatoms have the power of synthesising this factor when grown in sterilised sea-water in the light.

According to Harden (*loc. cit.*) the quantitative estimation of vitamin A in foodstuffs is best effected by the following experimental method: Young rats of about 50 grms. weight are fed on a diet lacking in vitamin A, for 3–4 weeks. They have then ceased to grow, usually at a weight not above 90 grms., and any which still continue to increase in weight are rejected. The substance to be tested is then added to the diet in varying amounts, a series of experiments with different groups of rats being made, and the minimum amount ascertained which will induce definite and continuous growth for a period of four weeks.

Whenever possible the experimental substance is administered quantitatively to the animals, usually before the rest of their ration. The results

obtained by Zilva and Miura in the estimation of vitamin A in a sample of cod-liver oil show the effect of gradually decreasing doses of cod-liver oil. Resumption of growth ceased between 1·4 and 1·7 mg., and 1·7 mg. was accordingly taken as the minimum daily dose of this sample of oil.

The caseinogen used in the basal diet for experiments of this kind may be purified by being heated on shallow trays in a current of air at 120° C. for 36 hours and repeatedly stirred during this time, to promote the oxidation of the vitamin A which is always found in crude caseinogen. This method is invariably successful, provided that a finely divided caseinogen is employed. Alternatively, the material may be thoroughly extracted first with warm alcohol and then with light petroleum. Wheat starch is generally employed and requires, as a rule, no purification. The best fat to use for the basal diet is refined hardened * cotton-seed oil, which has invariably been found to be completely inactive.

When animals are deprived of fat soluble A for any length of time an inflammatory condition of the eyes known as Xerophthalinia is set up which will ultimately lead to total blindness unless the substance be administered.

The vitamin A is soluble in fats and is extracted with them by such solvents as ether, alcohol, etc. It is also, however, soluble in water to a slight extent. It is probably not destroyed by heating to 120° in the absence of oxygen, but oxygenation particularly at temperatures above 80° soon destroys its activity. Reduction also is deleterious, particularly under certain conditions, but these have not yet been definitely established (cf. *J.S.C.I.*, 1925, 44, B609, B897).

The fat soluble A is not destroyed by heating with alkali and is left in the unsaponifiable matter when oils are saponified in the absence of air. It is not precipitated by digitonin so that this method suffices for separating it from the cholesterol. This method may be used for obtaining the substance in highly concentrated form, but isolation of the pure substance has not yet been brought about. The relation of sterols to vitamin A has been discussed by Drummond, Rosenheim and Coward (*J.S.C.I.*, 1925, 44, 123T).

L. S. Fridericia (*J.S.C.I.*, 1925, 44, B144) has observed that the addition of hydrogenated whale oil to a diet of which the vitamin A was supplied by butter fat rendered the diet insufficient for growth of rats, although the hydrogenated oil itself was shown to be without toxic effect; no such inactivation was observed with hydrogenated coconut or hemp-seed oils nor with non-hydrogenated coconut oil or abdominal fat from the pig; if, however, the latter fat were first heated to 105° in layers for twenty-four hours with free access of air, it acquired an inactivating action towards vitamin A; it is suggested that in this case the inactivating action may be due to the formation of peroxides in the heated fat.

This short account of fat-soluble A may be very usefully brought to a close with the following remarks of Harden's (*loc. cit.*):

" The close relation which exists between the presence of vitamin A in fats and the well-known reaction given by liver oils (which consists in the production of a purple colouration when the oil is dissolved in an organic solvent and a drop of sulphuric acid is added) has been pointed out by Drummond and Watson (1922). All the liver oils of mammals, birds, and fish examined by these authors gave the reaction, and it was also given, although less strongly, by the body fat of some animals and by butter. In striking agreement with the behaviour of vitamin A, the property of pro-

* The question as to whether this oil is quite safe has arisen. Some workers prefer to use oxygenated cotton-seed oil.

ducing the colouration is lost when a current of air is passed through the fat at 100° C., but not when the fat is heated at this temperature in the absence of air. Again, when the fat is hydrolysed it remains, with the vitamin A, in the unsaponifiable residue. Moreover, the intensity of the reaction was found to be roughly proportional to the vitamin A content of a series of fish-liver oils. The livers and fat of pigs and rats fed on diets deficient in vitamin A did not give the reaction, but this appeared when the deficiency was made good. It is obvious that there is a close parallel between the two properties, and the authors, without claiming that the test actually indicates the presence of the vitamin, suggest ' that the association may be of some significance.' The necessity for this caution is indicated by the facts that although the marine diatom Nitzschia has been shown to be rich in vitamin A, the oil extracted from this organism did not give the purple-colour test with sulphuric acid. A similar negative result was obtained with plankton oil, although the reaction in question is probably one between cholesterol or an analogous substance and some aldehydic compound (see Whitby, 1923; Harden and Robinson, 1923), but whether the latter is derived from the vitamin itself or not, is so far unknown."

Rosenheim and Drummond (*J.S.C.I.*, 1925, 44, B1008) have quite recently devised a further colour test which, it is suggested, is quite specific for the presence of vitamin A. It depends upon the blue colour which is produced on shaking arsenic chloride, methyl sulphate or trichloractic acid with a substance containing vitamin A, e.g. cod-liver oil. The reaction is also given by acetyl chloride and benzyl chloride in the presence of zinc chloride. The results so far obtained with this method are encouraging.

APPENDIX II

Refractive Indices of Aqueous Solutions of Chemically Pure Glycerol

Glycerol per cent.	Lenz. 12·5–12·8° C.	Strohmer. 17·5°.	Skalweit. 15° C.	Glycerol per cent.	Lenz. 12·5–12·8° C.	Strohmer. 17·5°.	Skalweit. 15° C.
100	1·4758	1·4727	1·4742	49	1·3993	..	1·3981
99	1·4744	1·4710	1·4728	48	1·3979	..	1·3966
98	1·4729	1·4698	1·4712	47	1·3964	..	1·3952
97	1·4715	1·4681	1·4698	46	1·3950	..	1·3938
96	1·4700	1·4670	1·4684	45	1·3935	..	1·3924
95	1·4686	1·4653	1·4670	44	1·3921	..	1·3910
94	1·4671	1·4636	1·4655	43	1·3906	..	1·3896
93	1·4657	1·4625	1·4640	42	1·3890	..	1·3882
92	1·4642	1·4608	1·4625	41	1·3875	..	1·3868
91	1·4628	1·4596	1·4610	40	1·3860	..	1·3854
90	1·4613	1·4579	1·4595	39	1·3844	..	1·3840
89	1·4598	1·4563	1·4580	38	1·3829	..	1·3827
88	1·4584	1·4551	1·4565	37	1·3813	..	1·3813
87	1·4569	1·4534	1·4550	36	1·3798	..	1·3799
86	1·4555	1·4523	1·4535	35	1·3785	..	1·3785
85	1·4540	1·4506	1·4520	34	1·3772	..	1·3771
84	1·4525	1·4489	1·4505	33	1·3758	..	1·3757
83	1·4511	1·4478	1·4490	32	1·3745	..	1·3743
82	1·4496	1·4461	1·4475	31	1·3732	..	1·3729
81	1·4482	1·4449	1·4460	30	1·3719	..	1·3715
80	1·4467	1·4432	1·4444	29	1·3706	..	1·3701
79	1·4453	1·4415	1·4429	28	1·3692	..	1·3687
78	1·4438	1·4398	1·4414	27	1·3679	..	1·3674
77	1·4424	1·4387	1·4399	26	1·3666	..	1·3660
76	1·4409	1·4370	1·4384	25	1·3652	..	1·3647
75	1·4395	1·4353	1·4369	24	1·3639	..	1·3633
74	1·4380	1·4336	1·4354	23	1·3626	..	1·3620
73	1·4366	1·4319	1·4339	22	1·3612	..	1·3607
72	1·4352	1·4308	1·4324	21	1·3599	..	1·3594
71	1·4337	1·4291	1·4309	20	1·3585	..	1·3581
70	1·4321	1·4274	1·4295	19	1·3572	..	1·3568
69	1·4304	1·4257	1·4280	18	1·3559	..	1·3555
68	1·4286	1·4240	1·4265	17	1·3546	..	1·3542
67	1·4267	1·4223	1·4250	16	1·3533	..	1·3529
66	1·4249	1·4206	1·4235	15	1·3520	..	1·3516
65	1·4231	1·4189	1·4220	14	1·3507	..	1·3503
64	1·4213	1·4167	1·4205	13	1·3494	..	1·3490
63	1·4195	1·4150	1·4190	12	1·3480	..	1·3477
62	1·4176	1·4133	1·4175	11	1·3467	..	1·3464
61	1·4158	1·4116	1·4160	10	1·3454	..	1·3452
60	1·4140	1·4099	1·4144	9	1·3442	..	1·3439
59	1·4126	1·4087	1·4129	8	1·3430	..	1·3426
58	1·4114	1·4070	1·4104	7	1·3417	..	1·3414
57	1·4102	1·4059	1·4099	6	1·3405	..	1·3402
56	1·4091	1·4048	1·4084	5	1·3392	..	1·3390
55	1·4079	1·4036	1·4069	4	1·3380	..	1·3378
54	1·4065	1·4019	1·4054	3	1·3367	..	1·3366
53	1·4051	1·4008	1·4039	2	1·3355	..	1·3354
52	1·4036	1·3997	1·4024	1	1·3342	..	1·3342
51	1·4022	1·3980	1·4010	0	..	..	1·3330
50	1·4007	1·3969	1·3996				

APPENDIX III

Specific Gravities of Aqueous Solutions of Chemically pure Glycerol

Glycerol per cent.	Lenz. 13°/12°.	Strohmer. 17·5°/17·5°.	Gerlach. 15°/15°.	Gerlach. 20°/20°.	Nicol. 20°/20°.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	..	..	1·18020
68	1·1826	1·176	..	..	1·17747
67	1·1795	1·173	..	..	1·17474
66	1·1764	1·170	..	..	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	..	..	1·16654
63	1·1671	1·160	..	..	1·16380
62	1·1640	1·157	..	..	1·16107

SPECIFIC GRAVITIES OF AQUEOUS SOLUTIONS OF CHEMICALLY PURE GLYCEROL—*continued*

Glycerol per cent.	Lenz.	Strohmer.	Gerlach.		Nicol.
	13°/12°.	17·5°/17·5°.	15°/15°.	20°/20°.	20°/20.°
61	1·1610	1·154	..	..	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	..	..	1·15288
58	1·1530	1·146	..	..	1·15015
57	1·1505	1·144	..	..	1·14742
56	1·1480	1·142	..	..	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	..	..	1·13923
53	1·1403	1·135	..	..	1·13650
52	1·1375	1·133	..	..	1·13377
51	1·1348	1·130	..	..	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	..	1·1155	1·1145	1·11469
40	1·1045	..	1·1020	1·1010	1·10118
35	1·0907	..	1·0885	1·0875	1·08786
30	1·0771	..	1·0750	1·0740	1·07469
25	1·0635	..	1·0620	1·0610	1·06166
20	1·0498	..	1·0490	1·0480	1·04884
15	1·0374	..	..	..	1·03622
10	1·0245	..	1·0245	1·0235	1·02391
5	1·0123	..	..	..	1·01184
0	1·0000	..	1·0000	1·0000	1·00000

APPENDIX IV

Viscosities of Glycerol Solutions (Archbutt and Deeley)

S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.	S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.
1·000	·01028	$\bar{2}$·01183	..	1·041	·01691	$\bar{2}$·22817	540
1·001	·01040	$\bar{2}$·01703	520	1·042	·01712	$\bar{2}$·23358	541
1·002	·01053	$\bar{2}$·02223	520	1·043	·01734	$\bar{2}$·23900	542
1·003	·01065	$\bar{2}$·02744	521	1·044	·01756	$\bar{2}$·24443	543
1·004	·01078	$\bar{2}$·03265	521	1·045	·01778	$\bar{2}$·24987	544
1·005	·01091	$\bar{2}$·03786	521	1·046	·01800	$\bar{2}$·25532	545
1·006	·01104	$\bar{2}$·04307	521	1·047	·01883	$\bar{2}$·26078	546
1·007	·01118	$\bar{2}$·04829	522	1·048	·01846	$\bar{2}$·26625	547
1·008	·01131	$\bar{2}$·05351	522	1·049	·01870	$\bar{2}$·27173	548
1·009	·01145	$\bar{2}$·05873	522	1·050	·01893	$\bar{2}$·27722	549
1·010	·01159	$\bar{2}$·06395	522	1·051	·01917	$\bar{2}$·28272	550
1·011	·01173	$\bar{2}$·06918	523	1·052	·01942	$\bar{2}$·28823	551
1·012	·01187	$\bar{2}$·07441	523	1·053	·01967	$\bar{2}$·29375	552
1·013	·01201	$\bar{2}$·07964	523	1·054	·01992	$\bar{2}$·29928	553
1·014	·01216	$\bar{2}$·08488	524	1·055	·02018	$\bar{2}$·30482	554
1·015	·01231	$\bar{2}$·09012	524	1·056	·02044	$\bar{2}$·31037	555
1·016	·01246	$\bar{2}$·09536	524	1·057	·02070	$\bar{2}$·31593	556
1·017	·01261	$\bar{2}$·10061	525	1·058	·02097	$\bar{2}$·32150	557
1·018	·01276	$\bar{2}$·10586	525	1·059	·02124	$\bar{2}$·32708	558
1·019	·01292	$\bar{2}$·11112	526	1·060	·02151	$\bar{2}$·33267	559
1·020	·01307	$\bar{2}$·11638	526	1·061	·02179	$\bar{2}$·33827	560
1·021	·01323	$\bar{2}$·12165	527	1·062	·02207	$\bar{2}$·34389	562
1·022	·01339	$\bar{2}$·12692	527	1·063	·02236	$\bar{2}$·34953	564
1·023	·01356	$\bar{2}$·13220	528	1·064	·02266	$\bar{2}$·35519	566
1·024	·01372	$\bar{2}$·13748	528	1·065	·02296	$\bar{2}$·36087	568
1·025	·01389	$\bar{2}$·14277	529	1·066	·02326	$\bar{2}$·36657	570
1·026	·01406	$\bar{2}$·14806	529	1·067	·02357	$\bar{2}$·37229	572
1·027	·01424	$\bar{2}$·15336	530	1·068	·02388	$\bar{2}$·37803	574
1·028	·01441	$\bar{2}$·15866	530	1·069	·02420	$\bar{2}$·38379	576
1·029	·01459	$\bar{2}$·16397	531	1·070	·02452	$\bar{2}$·38957	578
1·030	·01477	$\bar{2}$·16928	531	1·071	·02485	$\bar{2}$·39537	580
1·031	·01495	$\bar{2}$·17460	532	1·072	·02519	$\bar{2}$·40119	582
1·032	·01513	$\bar{2}$·17992	532	1·073	·02553	$\bar{2}$·40703	584
1·033	·01532	$\bar{2}$·18525	533	1·074	·02588	$\bar{2}$·41289	586
1·034	·01551	$\bar{2}$·19058	533	1·075	·02623	$\bar{2}$·41877	588
1·035	·01570	$\bar{2}$·19592	534	1·076	·02659	$\bar{2}$·42467	590
1·036	·01590	$\bar{2}$·20127	535	1·077	·02695	$\bar{2}$·43059	592
1·037	·01609	$\bar{2}$·20663	536	1·078	·02732	$\bar{2}$·43653	594
1·038	·01629	$\bar{2}$·21200	537	1·079	·02770	$\bar{2}$·44249	596
1·039	·01650	$\bar{2}$·21738	538	1·080	·02809	$\bar{2}$·44847	598
1·040	·01670	$\bar{2}$·22277	539	1·081	·02848	$\bar{2}$·45447	600

VISCOSITIES OF GLYCEROL SOLUTIONS—*continued*

S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.	S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.
1·082	·02887	$\bar{2}$·46049	602	1·129	·06038	$\bar{2}$·78090	792
1·083	·02928	$\bar{2}$·46653	604	1·130	·06150	$\bar{2}$·78889	799
1·084	·02969	$\bar{2}$·47259	606	1·131	·06265	$\bar{2}$·79695	806
1·085	·03011	$\bar{2}$·47867	608	1·132	·06384	$\bar{2}$·80508	813
1·086	·03053	$\bar{2}$·48478	611	1·133	·06506	$\bar{2}$·81328	820
1·087	·03097	$\bar{2}$·49092	614	1·134	·06631	$\bar{2}$·82156	828
1·088	·03141	$\bar{2}$·49709	617	1·135	·06760	$\bar{2}$·82992	836
1·089	·03186	$\bar{2}$·50329	620	1·136	·06892	$\bar{2}$·83836	844
1·090	·03232	$\bar{2}$·50952	623	1·137	·07029	$\bar{2}$·84688	852
1·091	·03279	$\bar{2}$·51578	626	1·138	·07169	$\bar{2}$·85548	860
1·092	·03327	$\bar{2}$·52207	629	1·139	·07314	$\bar{2}$·86416	868
1·093	·03376	$\bar{2}$·52839	632	1·140	·07463	$\bar{2}$·87292	876
1·094	·03426	$\bar{2}$·53474	635	1·141	·07617	$\bar{2}$·88177	885
1·095	·03476	$\bar{2}$·54112	638	1·142	·07775	$\bar{2}$·89071	894
1·096	·03528	$\bar{2}$·54753	641	1·143	·07939	$\bar{2}$·89974	903
1·097	·03581	$\bar{2}$·55397	644	1·144	·08107	$\bar{2}$·90886	912
1·098	·03635	$\bar{2}$·56044	647	1·145	·08281	$\bar{2}$·91807	921
1·099	·03689	$\bar{2}$·56694	650	1·146	·08460	$\bar{2}$·92737	930
1·100	·03745	$\bar{2}$·57347	653	1·147	·08645	$\bar{2}$·93676	939
1·101	·03802	$\bar{2}$·58003	656	1·148	·08836	$\bar{2}$·94625	949
1·102	·03860	$\bar{2}$·58662	659	1·149	·09033	$\bar{2}$·95584	959
1·103	·03920	$\bar{2}$·59324	662	1·150	·09237	$\bar{2}$·96553	969
1·104	·03980	$\bar{2}$·59989	665	1·151	·09448	$\bar{2}$·95732	979
1·105	·04042	$\bar{2}$·60657	668	1·152	·09665	$\bar{2}$·98521	989
1·106	·04105	$\bar{2}$·61329	672	1·153	·09890	$\bar{2}$·99520	999
1·107	·04169	$\bar{2}$·62005	676	1·154	·1012	$\bar{1}$·00529	1009
1·108	·04235	$\bar{2}$·62685	680	1·155	·1036	$\bar{1}$·01548	1019
1·109	·04302	$\bar{2}$·63369	684	1·156	·1061	$\bar{1}$·02578	1030
1·110	·04371	$\bar{2}$·64057	688	1·157	·1087	$\bar{1}$·03619	1041
1·111	·04441	$\bar{2}$·64749	692	1·158	·1114	$\bar{1}$·04671	1052
1·112	·04513	$\bar{2}$·65445	696	1·159	·1141	$\bar{1}$·05734	1063
1·113	·04586	$\bar{2}$·66146	701	1·160	·1170	$\bar{1}$·06808	1074
1·114	·04662	$\bar{2}$·66852	706	1·161	·1199	$\bar{1}$·07893	1085
1·115	·04738	$\bar{2}$·67563	711	1·162	·1230	$\bar{1}$·08989	1096
1·116	·04817	$\bar{2}$·68279	716	1·163	·1262	$\bar{1}$·10096	1107
1·117	·04898	$\bar{2}$·69000	721	1·164	·1295	$\bar{1}$·11215	1119
1·118	·04980	$\bar{2}$·69726	726	1·165	·1329	$\bar{1}$·12346	1131
1·119	·05065	$\bar{2}$·70457	731	1·166	·1364	$\bar{1}$·13489	1143
1·120	·05152	$\bar{2}$·71193	736	1·167	·1401	$\bar{1}$·14644	1155
1·121	·05240	$\bar{2}$·71935	742	1·168	·1439	$\bar{1}$·15811	1167
1·122	·05331	$\bar{2}$·72683	748	1·169	·1479	$\bar{1}$·16990	1179
1·123	·05425	$\bar{2}$·73437	754	1·170	·1520	$\bar{1}$·18181	1191
1·124	·05520	$\bar{2}$·74197	760	1·171	·1563	$\bar{1}$·19384	1203
1·125	·05619	$\bar{2}$·74963	766	1·172	·1607	$\bar{1}$·20600	1216
1·126	·05719	$\bar{2}$·75735	772	1·173	·1653	$\bar{1}$·21829	1229
1·127	·05823	$\bar{2}$·76513	778	1·174	·1701	$\bar{1}$·23071	1242
1·128	·05929	$\bar{2}$·77298	785	1·175	·1751	$\bar{1}$·24326	1255

VISCOSITIES OF GLYCEROL SOLUTIONS—*continued*

S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.	S.G. at 20°/20° C.	Viscosity at 20° C.	Log. of Viscosity.	Differences.
1·176	·1803	$\bar{1}$·25594	1268	1·220	·9195	$\bar{1}$·96356	2002
1·177	·1857	$\bar{1}$·26875	1281	1·221	·9635	$\bar{1}$·98383	2027
1·178	·1913	$\bar{1}$·28169	1294	1·222	1·010	0·00436	2053
1·179	·1971	$\bar{1}$·29476	1307	1·223	1·060	0·02516	2080
1·180	·2032	$\bar{1}$·30796	1320	1·224	1·112	0·04624	2108
1·181	·2096	$\bar{1}$·32130	1334	1·225	1·168	0·06761	2137
1·182	·2162	$\bar{1}$·33478	1348	1·226	1·228	0·08928	2167
1·183	·2231	$\bar{1}$·34840	1362	1·227	1·292	0·11126	2198
1·184	·2302	$\bar{1}$·36216	1376	1·228	1·360	0·13356	2230
1·185	·2377	$\bar{1}$·37606	1390	1·229	1·433	0·15619	2263
1·186	·2455	$\bar{1}$·39010	1404	1·230	1·511	0·17916	2297
1·187	·2537	$\bar{1}$·40428	1418	1·231	1·594	0·20248	2332
1·188	·2622	$\bar{1}$·41860	1432	1·232	1·683	0·22616	2368
1·189	·2711	$\bar{1}$·43307	1447	1·233	1·779	0·25021	2405
1·190	·2803	$\bar{1}$·44769	1462	1·234	1·882	0·27464	2443
1·191	·2900	$\bar{1}$·46246	1477	1·235	1·993	0·29946	2482
1·192	·3002	$\bar{1}$·47738	1492	1·236	2·112	0·32468	2522
1·193	·3108	$\bar{1}$·49245	1507	1·237	2·240	0·35031	2563
1·194	·3219	$\bar{1}$·50767	1522	1·238	2·379	0·37636	2605
1·195	·3335	$\bar{1}$·52304	1537	1·239	2·528	0·40284	2648
1·196	·3456	$\bar{1}$·53856	1552	1·240	2·690	0·42976	2692
1·197	·3583	$\bar{1}$·55424	1568	1·241	2·865	0·45711	2735
1·198	·3716	$\bar{1}$·57008	1584	1·242	3·054	0·48488	2777
1·199	·3856	$\bar{1}$·58608	1600	1·243	3·259	0·51306	2818
1·200	·4002	$\bar{1}$·60224	1616	1·244	3·481	0·54164	2858
1·201	·4155	$\bar{1}$·61857	1633	1·245	3·721	0·57061	2897
1·202	·4316	$\bar{1}$·63507	1650	1·246	3·981	0·59996	2935
1·203	·4485	$\bar{1}$·65174	1667	1·247	4·263	0·62969	2973
1·204	·4662	$\bar{1}$·66858	1684	1·248	4·569	0·65979	3010
1·205	·4848	$\bar{1}$·68559	1701	1·249	4·901	0·69025	3046
1·206	·5044	$\bar{1}$·70277	1718	1·250	5·261	0·72107	3082
1·207	·5250	$\bar{1}$·72013	1736	1·251	5·653	0·75224	3117
1·208	·5466	$\bar{1}$·73767	1754	1·252	6·078	0·78375	3151
1·209	·5694	$\bar{1}$·75539	1772	1·253	6·504	0·81560	3185
1·210	·5933	$\bar{1}$·77330	1791	1·254	7·043	0·84778	3218
1·211	·6186	$\bar{1}$·79140	1810	1·255	7·591	0·88029	3251
1·212	·6452	$\bar{1}$·80969	1829	1·256	8·187	0·91313	3284
1·213	·6733	$\bar{1}$·82818	1849	1·257	8·837	0·94630	3317
1·214	·7029	$\bar{1}$·84687	1869	1·258	9·546	0·97980	3350
1·215	·7341	$\bar{1}$·86577	1890	1·259	10·32	1·01363	3383
1·216	·7672	$\bar{1}$·88488	1911	1·260	11·16	1·04779	3416
1·217	·8021	$\bar{1}$·90421	1933	1·261	12·09	1·08228	3449
1·218	·8390	$\bar{1}$·92376	1955	1·262	13·10	1·11710	3482
1·219	·8781	$\bar{1}$·94354	1978				

APPENDIX V

Equivalents of Indices of Refraction and Butyro-Refractometer Readings

Refractive Index. n_D.	Fourth Decimal of n_D.									
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
	Scale Readings.									
1·422	0·0	0·1	0·2	0·4	0·5	0·6	0·7	0·9	1·0	1·1
1·423	1·2	1·4	1·5	1·6	1·7	1·9	2·0	2·1	2·2	2·4
1·424	2·5	2·6	2·7	2·8	3·0	3·1	3·2	3·3	3·5	3·6
1·425	3·7	3·8	4·0	4·1	4·2	4·3	4·5	4·6	4·7	4·8
1·426	5·0	5·1	5·2	5·4	5·5	5·6	5·7	5·9	6·0	6·1
1·427	6·2	6·4	6·5	6·6	6·8	6·9	7·0	7·1	7·2	7·4
1·428	7·5	7·6	7·7	7·9	8·0	8·1	8·2	8·4	8·5	8·6
1·429	8·7	8·9	9·0	9·1	9·2	9·4	9·5	9·6	9·8	9·9
1·430	10·0	10·1	10·3	10·4	10·5	10·6	10·7	10·9	11·0	11·1
1·431	11·3	11·4	11·5	11·6	11·8	11·9	12·0	12·2	12·3	12·4
1·432	12·5	12·7	12·8	12·9	13·0	13·2	13·3	13·5	13·6	13·7
1·433	13·8	14·0	14·1	14·2	14·4	14·5	14·6	14·7	14·9	15·0
1·434	15·1	15·3	15·4	15·5	15·6	15·8	15·9	16·0	16·2	16·3
1·435	16·4	16·6	16·7	16·8	17·0	17·1	17·2	17·4	17·5	17·6
1·436	17·8	17·9	18·0	18·2	18·3	18·4	18·5	18·7	18·8	18·9
1·437	19·1	19·2	19·3	19·5	19·6	19·7	19·8	20·0	20·1	20·2
1·438	20·4	20·5	20·6	20·8	20·9	21·1	21·2	21·3	21·4	21·6
1·439	21·7	21·8	22·0	22·1	22·2	22·4	22·5	22·6	22·7	22·9
1·440	23·0	23·2	23·3	23·4	23·5	23·7	23·8	23·9	24·1	24·2
1·441	24·3	24·5	24·6	24·7	24·8	25·0	25·1	25·2	25·4	25·5
1·442	25·6	25·8	25·9	26·1	26·2	26·3	26·5	26·6	26·7	26·9
1·443	27·0	27·1	27·3	27·4	27·5	27·7	27·8	27·9	28·1	28·2
1·444	28·3	28·5	28·6	28·7	28·9	29·0	29·2	29·3	29·4	29·6
1·445	29·7	29·9	30·0	30·1	30·3	30·4	30·6	30·7	30·8	30·9
1·446	31·1	31·2	31·4	31·5	31·6	31·8	31·9	32·1	32·2	32·3
1·447	32·5	32·6	32·8	32·9	33·0	33·2	33·3	33·5	33·6	33·7
1·448	33·9	34·0	34·2	34·3	34·4	34·6	34·7	34·9	35·0	35·1
1·449	35·3	35·4	35·6	35·7	35·8	36·0	36·1	36·3	36·4	36·5
1·450	36·7	36·8	37·0	37·1	37·2	37·4	37·5	37·7	37·8	37·9
1·451	38·1	38·2	38·3	38·5	38·6	38·7	38·9	39·0	39·2	39·3
1·452	39·5	39·6	39·7	39·9	40·0	40·1	40·3	40·4	40·6	40·7
1·453	40·9	41·0	41·1	41·3	41·4	41·5	41·7	41·8	42·0	42·1
1·454	42·3	42·4	42·5	42·7	42·8	43·0	43·1	43·3	43·4	43·6
1·455	43·7	43·9	44·0	44·2	44·3	44·4	44·6	44·7	44·9	45·0
1·456	45·2	45·3	45·5	45·6	45·7	45·9	46·0	46·2	46·3	46·4
1·457	46·6	46·7	46·9	47·0	47·2	47·3	47·5	47·6	47·7	47·9
1·458	48·0	48·2	48·3	48·5	48·6	48·8	48·9	49·1	49·2	49·4
1·459	49·5	49·7	49·8	50·0	50·1	50·2	50·4	50·5	50·7	50·8

EQUIVALENTS OF INDICES OF REFRACTION AND BUTYRO-REFRACTOMETER READINGS—*continued*

Refractive Index. n_D.	Fourth Decimal of n_D.									
	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
	Scale Readings.									
1·460	51·0	51·1	51·3	51·4	51·6	51·7	51·9	52·0	52·2	52·3
1·461	52·5	52·7	52·8	53·0	53·1	53·3	53·4	53·6	53·7	53·9
1·462	54·0	54·2	54·3	54·5	54·6	54·8	55·0	55·1	55·3	55·4
1·463	55·6	55·7	55·9	56·0	56·2	56·3	56·5	56·6	56·8	56·9
1·464	57·1	57·3	57·4	57·6	57·7	57·9	58·0	58·2	58·3	58·5
1·465	58·6	58·8	58·9	59·1	59·2	59·4	59·5	59·7	59·8	60·0
1·466	60·2	60·3	60·5	60·6	60·8	60·9	61·1	61·2	61·4	61·5
1·467	61·7	61·8	62·0	62·2	62·3	62·5	62·6	62·8	62·9	63·1
1·468	63·2	63·4	63·5	63·7	63·8	64·0	64·2	64·3	64·5	64·7
1·469	64·8	65·0	65·1	65·3	65·4	65·6	65·7	65·9	66·1	66·2
1·470	66·4	66·5	66·7	66·8	67·0	67·2	67·3	67·5	67·7	67·8
1·471	68·0	68·1	68·3	68·4	68·6	68·7	68·9	69·1	69·2	69·4
1·472	69·5	69·7	69·9	70·0	70·2	70·3	70·5	70·7	70·8	71·0
1·473	71·1	71·3	71·4	71·6	71·8	71·9	72·1	72·2	72·4	72·5
1·474	72·7	72·9	73·0	73·2	73·3	73·5	73·7	73·8	74·0	74·1
1·475	74·3	74·5	74·6	74·8	75·0	75·1	75·3	75·5	75·6	75·8
1·476	76·0	76·1	76·3	76·5	76·7	76·8	77·0	77·2	77·3	77·5
1·477	77·7	77·9	78·1	78·2	78·4	78·6	78·7	78·9	79·1	79·2
1·478	79·4	79·6	79·8	80·0	80·1	80·3	80·5	80·6	80·8	81·0
1·479	81·2	81·3	81·5	81·7	81·9	82·0	82·2	82·4	82·5	82·7
1·480	82·9	83·1	83·2	83·4	83·6	83·8	83·9	84·1	84·3	84·5
1·481	84·6	84·8	85·0	85·2	85·3	85·5	85·7	85·9	86·0	86·2
1·482	86·4	86·6	86·7	86·9	87·1	87·3	87·5	87·6	87·7	88·0
1·483	88·2	88·3	88·5	88·7	88·9	89·1	89·2	89·4	89·6	89·8
1·484	90·0	90·2	90·3	90·5	90·7	90·9	91·1	91·2	91·4	91·6
1·485	91·8	92·0	92·1	92·3	92·5	92·7	92·9	93·0	93·2	93·4
1·486	93·6	93·8	94·0	94·1	94·3	94·5	94·7	94·8	95·0	95·2
1·487	95·4	95·6	95·8	96·0	96·1	96·3	96·5	96·7	96·9	97·0
1·488	97·2	97·4	97·6	97·8	98·0	98·1	98·3	98·5	98·7	98·9
1·489	99·1	99·2	99·4	99·6	99·8	100·0	..	..	..	..

APPENDIX VI

Standardisation of Viscometers

Prepare eight solutions of purest glycerin in distilled water by weighing the glycerin carefully and thoroughly mixing together. The solutions are placed in stoppered bottles, 250 c.c. of each being a suitable quantity.

						Per cent.
(I.)	Glycerol 110 grms.	make up to	250 c.c.	with	water	(44·0)
(II.)	„ 142·5	„	„	„	„	(56·9)
(III.)	„ 165	„	„	„	„	(66·0)
(IV.)	„ 177·4	„	„	„	„	(71·0)
(V.)	„ 188·2	„	„	„	„	(75·3)
(VI.)	„ 201	„	„	„	„	(80·4)
(VII.)	„ 227	„	„	„	„	(90·8)
(VIII.)	„ 237	„	„	„	„	(94·8)

APPENDIX VII

Notes on Recently Published Work

Rancidity (Page 7)

J. Bulir (*B.C.A.*, 1926, 1, B66) suggests the use of α-diaminodiphenylamine sulphate as a test for rancidity in fats. He considers the following to be better: Shake 1 c.c. of the fat dissolved in light petroleum with 2 c.c. of 20 per cent. alcoholic potassium iodide solution, add 15 c.c. of water, shake, and test the aqueous layer with starch paste. A blue colour indicates that the fat is rancid.

The Drying of Oils (Page 9)

L. Auer (*B.C.A.*, 1926, 1, B450) shows that linseed oil " dried " in an atmosphere of carbon dioxide or in a " vacuum " increased in weight, but not in the vacuum produced by a mercury pump, whilst H. Wolff (*ibid.*) considers that, as linseed oil varnishes dry in an atmosphere containing so little oxygen, the drying process is essentially of colloidal type, and is possibly independent of the oxidation reaction. G. F. A. Stutz, H. A. Nelson, and F. S. Schmutz (*ibid.*, 20) consider that during drying on exposure to light oils evolve hydrogen peroxide. The composition of the films of polymerised oils is dealt with by V. J. Marcusson (*ibid.*, 500).

Fatty Acids (Pages 28-35)

Barium Salts (pages 28 and 39).—The following solubilities of barium stearate and barium ricinoleate have been found by K. Inokuchi (*B.C.A.*, 1926, 1, B285).

Solubility in absolute alcohol in grms. per 100 grms.

Temperature °C.	Ba. Stearate.	Ba. Ricinoleate.
10	trace	0·06
20	trace	0·13
30	trace	0·33
40	0·014	2·00
50	0·018	9·37
60	0·024	28·19

Solubility in alcohol (*d* 15°/4° 0·8119) of barium stearate

Temperature °C.	Solubility grms. per 100 grms.
20	trace
30	0·011
40	0·017
50	0·022
60	0·029

Arachidic Acid (page 30).—W. D. Cohen (*B.C.A.*, 1926, 1, B98) finds that the arachidic acid of arachis oil has M.Pt. 74·5°-75° and he finds in addition a C_{24} acid having M.Pt. 80°-80·5° which probably has a straight carbon chain. No C_{22} acid was found (cf. Ehrenstein and Stuewer, *J.S.C.I.*, 1923, 42, 1031). D. Holde and N. N. Godbole (*B.C.A.*, 1926, 1, A268, 498) find that arachis oil contains a hexacosoic acid $C_{26}H_{52}O_2$ having M.Pt. 79°, which is possibly identical with the cerotic acid from beeswax. They further isolated lignoceric acid, $C_{24}H_{48}O_2$, having M.Pt 80·5°-81·0°.

Erucic Acid (page B35).—A. W. Thomas and M. Mattikow (*Analyst*, 1926, 51, 315) suggest the separation of erucic acid from rape oil by means of the magnesium salt. They also give a laboratory method of hydrogenating erucic acid to behenic acid.

Miscellaneous References

The following papers have also been published :

R. L. Shriner and R. Adams (*B.C.A.*, 1926, 1, A47). " The Structure of Chaulmoogric Acid."

" Iso-oleic Acid and Other Unsaturated Fatty Acids Formed by Distillation of α-Hydroxystearic Acid. V. Vesely and H. Majtl (*B.C.A.*, 1926, 1, A47).

" Glycerol-Phosphoric Acids from Lecithin." P. Karrer and H. Salomon (*ibid.*, 384A).

" Preparation of Triacetin." S. Kawai (*ibid.*, 281A).

" Ethyl β-Hydroxybutyrate." A. Dewael (*ibid.*, 384A).

A. Grun and W. Czerny (*ibid.*, 269A). " Preparation and Properties of Octadecenoic Acids."

" Oxidation of α and β-Hydroxybutyric Acids with Hydrogen Peroxide." E. J. Witzemann (*ibid.*, 270A).

" Resolution of Glycerol α-Phosphoric Acid." P. Karrer and P. Benz (*ibid.*, 383A).

The Sterols (Page 40)

J. V. Steinle and L. Kahlenberg (*Analyst*, 1926, 51, 310) suggest the detection and colourimetric determination of cholesterol and phytosterol together by means of a chloroform solution of antimony pentachloride, which forms a muddy brown precipitate soluble in excess of chloroform, and which solution, on exposure to light, yields a cobalt-blue solution.

Separation of Fatty Acids (Page 61)

The surface tension of fatty acids in benzine solution in contact with dilute soda solutions is stated by R. Dubrisay (*B.C.A.*, 1926, 1, B99) to distinguish readily between pure acids and mixtures having the same refraction.

Liebermann-Storch Test (Page 79)

H. Wolff (*ibid.* 66) states that linseed oil giving a pseudo Liebermann-Storch reaction may be distinguished from those adulterated with rosin oil by the fact that the violet colour is produced immediately by the latter, and after a longer time, especially after passing through brown and red, by the former.

Qualitative and Quantitative Tests

Unsaponifiable Matter (page 120).—The American methods for this test have lately been compared (*J.O.F.I.*, 1926, 3, 64). D. Holde and A. Gorgas (*B.C.A.*, 1926, 1, B98) have pointed out a possible source of error in using the qualitative test for unsaponifiable matter, especially in fish oils, and suggest the addition of water drop by drop to the alcoholic soap solution.

Colour.—An American Committee has published suggested methods for determining the colour of cotton-seed and other vegetable oils (*J.O.F.I.*, 1926, 3, 189).

Acid Value (page 116).—T. Hidaker (*ibid.*, p. B199) states that the oil should be emulsified with water and then filtered before the acid value is determined. He names the acid value of the treated oil, the " real acid value " and the value obtained by subtracting this from the acid value of the untreated oil he describes as the " impure acid value."

A rapid method for the determination of free fatty acids in cotton-seed oil is given by H. B. Battle (*J.O.F.I.*, 1926, 3, 169).

Iodine Value (page 137).—A large quantity of work is still being published on slight variations in the various standard methods. The following papers may be consulted : *B.C.A.*, 1926, 1, B20, 199, 414, 447, 499.

H. P. Kaufmann (*ibid.*, 447) suggests the use of $N/_{10}$ solution of bromine in absolute methyl alcohol saturated with sodium bromide.

It is pointed out by B. M. Margosches and H. Fuchs (*ibid.*, 371) that the natural variations in the iodine value and " upper iodine " value (page 141 *supra*) are quite parallel so that the difference between these, only varies within narrow limits, and is characteristic for each fat.

Thiocyanogen Value (page 144).—Further work on this method has now been published (*Analyst*, 1926, 51, 157, 264). It is stated that the most suitable solvent is glacial acetic acid obtained by distilling a good commercial glacial acid (at least 99 per cent.) over phosphoric anhydride and collecting for use the fraction 118°-120°. The distillate being received in a vessel having a calcium chloride seal. The reagent is prepared by dividing the prepared acetic acid into two equal portions, to one of which is added (in absolutely dry glass stoppered vessels) the calculated amount of bromine (plus 5 per cent. excess) to give a solution of the required normality (0·1-0·05N).

In the second flask is suspended the quantity of pure lead thiocyanate (previously dried over phosphoric pentoxide) to react with the bromine in the other flask (plus 50 per cent. excess)—$Pb(SCN)_2 + Br_2 = PbBr_2 + (SCN)_2$. The bromine solution is added, with continual shaking, to the acid in which the lead thiocyanate is suspended, and the mixing continued until decolorisation is complete, after which the solution of free thiocyanogen is filtered through a dry filter from the lead bromide and excess of lead thiocyanate. It is standardised by adding a measured volume of it to potassium iodide solution (not vice-versa, or hydrolysis occurs), and titrating the liberated iodine with thiosulphate. To prevent polymerisation of the thiocyanogen the solution should be kept in the dark, and restandardised before use. The method of carrying out the process is as follows : A weighed quantity (0·1 to 0·2 grm.) of the oil is dissolved in sufficient 0·1N or 0·05N solution of the reagent to give an excess of 100 to 500 per cent. of thiocyanogen. After the absorption (5 to 15 hours according to the oil) the mixture is poured into an excess of an aqueous solution of potassium iodide, and the liberated iodine titrated. Simultaneously a blank determination is made

with the thiocyanogen solution under the same conditions. For comparison, the results are expressed as iodine values.

It has been found that with oleic, erucic and brassidic acids the results agree with the Hanus method but that with fatty acids containing a triple bond there was no absorption of thiocyanogen, whilst trilinolin gave a value equal to half the Hanus value, the same result being obtained for elæostearin. The method has been used to determine the amount of linolic acid in various oils as follows: Castor oil, 1·2; olive oil, 4·9; arachis oil (five samples), 22·5; 23·1, 10·1, 18·6, 19·8; almond oil (2 samples), 16·0, 14·8; rape oil, 33·1; Cacao butter, 0·0; coconut oil, 0·0; poppy-seed oil, 63·8· sesamé oil (4 samples), 38·8; 37·8; 35·0; 36·5.

Individual Oils

Poppy-Seed Oil (page 181).—The seeds of the opium poppy have been found by H. E. Annett and M. N. Bose (*B.C.A.*, 1926, 1, B66) to contain about 50 per cent. of fat calculated on the dry seeds.

Soya-Bean Oil (page 188).—The composition of a sample of soya-bean oil has been found by H. Pfahler (*ibid.*, 413) to have the following composition: linolenic acid, 1·9 per cent.; linoleic acid, 29·2 per cent.; isolinoleic acid, 24·3 per cent.; oleic acid, 30·8 per cent.; stearic acid, 7·0 per cent.; palmitic acid, 2·4 per cent.

Cotton-Seed Oil (page 212).—The following papers on cotton-seed oil appear in Volume III of the *Journal of Oil and Fat Industries:*

"The Keeping Quality of Crude Cotton-Seed Oil." G. S. Jamieson and W. F. Baughman. Page 75.

"A Method for the Analysis of Cotton-Seed." C. H. Cox. Page 125, cf. page 34, 197, 209.

"Determination of Lint in Cotton-Seed." T. L. Rettger. Page 135.

"Constituents of Crude Cotton-Seed Oil." G. S. Jamieson. Page 153.

"The Proteins of Cotton-Seed." D. Wesson. Page 165.

"Results of Cotton-Seed Meal Feeding Investigations." Page 170.

"Gossypol and Cotton-Seed Meal Poisoning." E. W. Schwartze. Page 173.

"Oil and Ammonia Content of Varieties of Cotton-Seed." A. F. Sievers and M. S. Lowman. Page 191.

"Determination of Moisture in Cotton-Seed Meal." Page 193.

Olive Oil (page 267).—Papers on the preparation and properties of "sulphur" olive oil are given by G. H. P. Trevithick with M. F. Lauro and W. H. Dickhart (*J.O.F.I.*, 1926, 3, 77, 128).

A sample of Spanish olive oil (iodine value 82·7) was found by K. Täufel and J. G. Sarria (*B.C.A.*, 1926, 1, B332) to contain stearic acid, 2·3 per cent.; palmitic acid, 7·6 per cent.; oleic acid, 83·9 per cent.; and linoleic acid, 0·5 per cent. Arachidic acid was not found whilst triolein and α-palmitodiolein were isolated.

Oil of Datura Alba.—The seeds of *Datura Alba* yield about 13 per cent. of oil on extraction (H. Dieterle, *B.C.A.*, 1926, 1, B372). The characteristics and composition of the oil are given.

Shea Butter (page 295).—R. Ehrenstein (*Analyst*, 1926, 51, 40) found the fatty acids of shea butter to have M.Pt. 55·5° C. and iodine value 50·8 and that they consist practically solely of stearic and oleic acids. The

unsaponifiable portion of the butter contains a phytosterol, M.Pt. 149° C. together with alcohol-soluble and alcohol insoluble constituents, having the respective formulæ $C_{42}H_{72}O_3$ and $C_{84}H_{144}O_6$. The polymerisation of the former into the latter proceeds spontaneously and is accelerated by rise of temperature; it is accompanied by disappearance of the linking C: C. The acetyl values of both of these constituents are about 90 and relate only to secondary alcoholic groups.

Cacao Butter (page 301.)—T. Sabalitschka (*B.C.A.*, 1926, 1, B20) confirms the necessity of keeping cacao butter several weeks after melting before the M.Pt. is taken. He prefers Welman's method (*Pharm. Ztg.*, 1900, 45, 959) or some method which does not require the fat to be melted before the test is supplied. H. Fincke (*ibid.*, 73B) states that the smaller cacao beans contain a smaller percentage of fat and more husk and germ than usual. The husk fat was found to be very acid. The germ fat had a low saponification value and an unpleasant taste. It is suggested that the presence of these fats in cacao butter is indicated by increased fibre content and acidity of the fat. J. Hanus and B. Komorosova and J. Lukas (*ibid.*, B140), recommend the ethyl ester value for the detection of coconut oil in cacao butter although it is difficult to see the advantage of this over the Polenske method.

Coconut Oil (page 323).—H. I. Watermann and H. J. Rijkes (*B.C.A.*, 1926, 1, B499) have distilled coconut oil at a pressure of 0·003 mm. Four fractions were collected at 208°-218°, 218°-223°, 223°-232°, 232°-259°. Practically no decomposition occurred. (Cf. Caldwell and Hurtley, *supra*, page 330.)

Ox-Liver Oil.—This oil has been examined by K. Kimura (*B.C.A.*, 1926, 1, B285), characteristics and composition are given.

Butter Fat in Margarine (page 411).—J. Kuhlmann and J. Grossfeld (*Analyst*, 1926, 51, 305) extend the "salting out" process of Gilmour (*ibid.*, 1925, 40, 276) by the addition of coconut oil soaps, in the following way: Five grms. of the fat are saponified with 2 c.c. of potassium hydroxide solution (750 grms. KOH per litre) and 10 c.c. of glycerin, and the soap solution cooled below 100° C., and diluted with 100 c.c. of water. The liquid is then cooled to 20° C., treated with 50 c.c. of dilute sulphuric acid (25 c.c. H_2SO_4 per litre) 15 grms. of powdered anhydrous sodium sulphate, 10 c.c. of coconut soap solution (pure coconut oil (100 grms.) is saponified by heating it with 100 grms. of glycerin and 40 grms. of potassium hydroxide solution (750 grms. per litre) and the solution, when cold, is made up to a litre), and a pinch (about 0·1 grm.) of purified kieselguhr. The flask is then repeatedly shaken, allowed to stand for 10 minutes or longer, its contents filtered through a dry filter, and 125 c.c. of the clear filtrate distilled (after addition of a little pumice-stone) until 110 c.c. of distillate have been obtained in a period of 20 minutes. This distillate is titrated (without filtration) with 0·1 N sodium hydroxide solution, phenolphthalein being used as indicator. A blank determination, without the fat, but with 10 c.c. of the coconut soap solution, is made, and the difference between the number of c.c. of alkali in the two determinations calculated on 5 grms. of the fat, and expressed in terms of 0·1 N solution, is termed the "butyric acid value."

Butter fat gives figures between 18·6 and 23·0 (average 20·3) whilst coconut oil gives 0·8-1·0 (average 0·9). J. Grossfield in a later paper (*B.C.A.*, 1926, 1, B447) states that the ratio between the factor for butter fat and coconut oil by this process is 81,* as compared with 3·8 for the Reichert value and 12 for his "B" value. The probable content of butter fat in a

* This is not borne out by the figures given e.g., 20·3 for butter and 0·9 for coconut oil.

mixture having butyric acid value and saponification value (less 200) is given by

$$M = 5{\cdot}115 - 0{\cdot}085.$$ (Cf. *ibid.*, 252, 499.)

S. H. Bertram, J. P. K. Van der Steur and F. Verhagen (*ibid.*, 140) determine coconut oil and butter fat in margarine by means of the following process: The fat is saponified by means of glycerol potash, the soap diluted with water, and the insoluble magnesium soaps precipitated at 70-80° by means of magnesium sulphate and filtered off. One part of the filtrate is treated with sodium and silver nitrate and the amount of insoluble silver salts so produced determined by means of back titration with thiocyanate. The volatile acids are determined in the second part by a modified Kirschner method when the percentage of butter and coconut oil are obtained by reference to a standard chart. Cf. C. J. Kuhlmann and J. Grossfeld (*ibid.*, 165), where practical details are given.

W. Normann (*J.O.F.I.*, 1926, 3, 70) has patented a process by which a butter substitute is prepared by heating a hardened fat with butyric acid. Cf. Patterson and Dickinson (*J.C.S.*, 1901, 79, 280).

Marine Oils (page 435).—M. Tsujimoto (*Analyst*, 1926, 51, 49) finds in shark liver oil acids having the formulæ $C_{24}H_{48}O_2$ (M.Pt. 78° " Selachoceric " acid) and $C_{24}H_{46}O_2$ (M.Pt. 43° " Selacholeic " acid). On hydrogenation a saturated acid differing from " Selachoceric " acid (M.Pt. 82·0°) is formed. Nitrous acid changes " Selacholeic " acid into the stereoisomeric " Selachelaidic " acid (M.Pt. 60·5°).

The following data have been obtained by examination of the oils from sharks and rays. A. Rogers (*B.C.A.*, 1926, 1, B19). Sand shark, $d^{25.5°}$ 0·9216, $n^{15.5°}$ 1·4761, iodine value, 130·4, saponification value 186, unsaponifiable matter 0·83 per cent. Tiger shark, $d^{25.5°}$ 0·9104, $n^{15.5°}$ 1·4711, iodine value, 94·1, sapon. value, 176, unsaponifiable matter, 1·71 per cent. Hammerhead shark, $d^{25.5°}$ 0·9218, $n^{15.5°}$ 1·4760, iodine value, 129·7, sapon. value, 184·7, unsaponifiable matter, 0·62 per cent. Nurs shark, $d^{25.5°}$ 0·9184, $n^{15.5°}$ 1·4716, iodine value, 108·3, sapon. value, 188·6, unsaponifiable matter, 0·41 per cent. Devil fish, $d^{25.5°}$ 0·9307, $n^{15.5°}$ 1·4840, iodine value, 166·3, saponification value, 186·3, unsaponifiable matter, 5·16 per cent. Saw fish, $d^{25.5°}$ 0·9220, $n^{15.5°}$ 1·4768, iodine value, 139·2, saponification value, 184·5, unsaponifiable matter, 0·91 per cent.

Dugong Oil (page 442).—A sample of this oil examined at the Imperial Institute (*Analyst*, 1926, 51, 150) had the following characteristics: Sp. gr. at 15° C., 0·9242; $n_D^{40°}$, 1·458; rotary power at 40° C., −0·12°; titre, 34·6°; acid value, 0·3, saponification value, 204·7; iodine value (Hübl, 17 hours), 52·3; unsaponifiable matter, 0·2 per cent., and volatile acids (soluble), 0·3 (insoluble 1·6 as c.c. of 0·1 N alkali solution required to neutralise 5 grms. of oil.

The effect of " blowing " on fish oils and other oils has been studied by C. H. Thomson (*Analyst*, 1926, 51, 177).

Chaulmoogra Oil (page 461).—E. André (*Analyst*, 1926, 51, 90) considers that the optical activity of oils of this group is not entirely due to the presence of chaulmoogric and hydnocarpic acids. He gives the following figures as representing various commercial oils.

Source.	Sp. gr. at 32° C.	Refract. Index at 29° C.	$[\alpha]_D$.	M.Pt. °C.	Sap. Value.	Iodine Value (Hanus)
Taraktogenos kurzii . .	0·9425	..	+48°0	33/39	210·4	96·1
Hydnocarpus anthelmintica	0·9447 (29°)	1·4755	+58°10	26/29	191·0	90·0
,, ,,	0·9427	1·4742	+48°0	25/26	187·3	88·3
Hydnocarpus wightiana .	0·9330	1·4780	+61°40	28/32	197·2	103·0
Hydnocarpus alpina . .	0·9346	1·4764	+57°0	20·5	201·0	95·0
Asteriastigma macrocarpa	0·9217	1·4725 *	+44°0	37/39	189·4	82·8
Oncoba echinata . . .	0·9286	1·4740 †	+56°10	41	184·5	98·0
Carpotroche Brasiliensis .	0·9499	1·4755 †	+53°40	21/23	183·7	106·1

Effect of Diet on Fat of Animals (Pages 369, 400)

Paraschtschuk (*B.C.A.*, 1926, I, B73) states that the increase in the Polenske value of the butter, which follows addition of coconut-oil cake to the ration, is much less when the cows are in poor condition than when they are in normal condition.

N. R. Ellis and O. G. Hankins (*Analyst*, 1926, 51, 153) have studied the effect of a diet consisting of food containing a somewhat hard fat (corn fat) on the body fat of hogs. They find that (1) The change from a soft fat as found in young, immature hogs, to a hard fat in older, mature hogs, was accompanied by an increased rate of fat deposition. (2) This increased rate of fat deposition caused a rise in the ratio of body fat derived from carbohydrate and protein (hard) to that derived from ingested fat (soft). (3) The change in the composition of the body fat resulted in a decrease in the iodine value and refractive index and an increase in the melting-point. (4) The effects on the proportions of the fatty acids were: An increase in the per cent. of total saturated acids with the per cent. of oleic acid remaining nearly constant and a decrease in the per cent. of linolic acid. The total amount of linolic acid ingested was in excess of that in the body in late, as well as early, growth. It has been shown that linolic acid in the body of hogs follows the supply in the feed very closely. Its actual percentage varies through extremely wide limits. Linolic acid is not so essential a factor as oleic acid in adipose tissue. The drop in the per cent. of linolic acid in the fat, with the corresponding rise in the per cent. of saturated acids, explains the hardening of the fats.

J. F. Geisler (*J.O.F.I.*, 1926, 3, 115) finds that a cotton-seed cake feed decreases the Reichert value and increases the melting-point and iodine value of the butter fat.

Vitamins (Page 477)

R. Hoagland and G. G. Snider (*Analyst*, 1926, 51, 311) find that there is a tendency for yellow oleo-oils and stearines to contain more vitamin-A than those of paler colour. W. C. Powick (*B.C.A.*, 1926, I, B382) has shown that rancid lard seems to inactivate vitamin-A.

O. Rosenheim and J. C. Drummond (*Analyst*, 1926, 51, 93) give the following details for carrying out their colour test: One c.c. of pure arsenic chloride is added from a 1 c.c. pipette to one drop of cod-liver oil in a test-

* At 25°. † At 31°.

tube and shaken. The oil dissolves to form a blue solution which assumes a purple tint in a few seconds and gradually fades. The reaction is characterised by a well-defined absorption band (λ 550-590), which persists for about 5 minutes. A one per cent. solution in petroleum spirit of a highly growth-promoting Newfoundland cod-liver oil was found to react intensely with 1 c.c. of arsenic chloride in amounts of 0·05 c.c. (0·5 mg.) of oil. The limit was reached with 5 cmm. (=0·05 mg.), measured with a Wright's capillary pipette. A suitable colour standard for the arsenic chloride reaction is a mixture of 100 c.c. of crystal violet solution, 1: 10,000 with 50 c.c. of methylene blue solution of the same strength (both in alcohol). The colour produced by 20 mg. of the Newfoundland oil (=1 drop from a pointed glass rod of 3 mm. diameter) with 1 c.c. of arsenic chloride matched the standard dye solution diluted in the proportion 3: 2.

W. R. Fearon (*ibid.*, 311) finds that it is not possible to isolate vitamin-A by means of the colour reaction with phosphorous pentoxide. J. C. Drummond, H. J. Channon, and K. H. Coward (*Analyst*, 1926, 1, 312) consider that little success has yet followed attempts to isolate vitamin-A, and they criticise Takahashi's claims to have isolated this substance as an unsaturated alcohol $C_{27}H_{44}O_2$ (" biosterin ") having the following characteristics: $d^{15°}$ 0·9561; $n^{20°}$ 1·52517; optically inactive; B.P., 147° at 0·2 mm.; Mol. Wt., 375 approx.; iodine value, Wijs, 178; acetyl value, 137; 0·001 mg., maintains health in rats for several weeks and doses greater than 10 mg. are toxic (*J.S.C.I.*, 1925, 44, B860).

H. W. Southgate (*Analyst*, 1926, 51, 94) has shown that when cod-liver oil is slowly heated out of contact with air to 300° C. the anti-rachitic and growth-promoting factors contained in it appear to be completely destroyed. If it is slowly heated to 200° C. and maintained at this temperature for some hours these two factors slowly disappear *pari passu*. Oxidation from external sources is unnecessary for the destruction of these factors at these temperatures. If oxygen is excluded, the chemical compound (or compounds) representing these factors is fairly stable to heat.

Miscellaneous References

" The Rapid Determination of Oils in Oil-Seeds," H. C. Fellows. *J.O.F.I.*, 1926, 3, 112.

" Digestibility of Animal Fats," A. D. Holmes. *J.O.F.I.*, 1926, 3, 11.

" Environment Factors affecting Proteins and Oil Contents of Soya-Beans," and the " Iodine Value of Soya-Bean Oil." *J.O.F.I.*, 1926, 3 40.

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